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THE STRUCTURE AND OPTICAL BEHAVIOUR OF THE CEYLON MOONSTONES

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1. Introduction

As is well known, the commonly occurring feldspars have a chemical composition which may be represented as a mixture of three components, namely the potash, soda and lime feldspars. The first two components resemble each other chemically but have different crystal forms, while the second and third components are isomorphous though their chemical formulæ are dissimilar. The question arises whether the feldspars formed by such admixture are in all cases truly homogeneous crystals. Optical studies may well be expected to throw some light on this issue. In a recent paper in these *Proceedings*,[1] it has been shown that the iridescence exhibited by labradorite results from the segregation of the potash feldspar present in the mineral from the isomorphous mixture of the soda and lime feldspars which are its principal constituents. Tiny crystals of orthoclase are formed as the result of such segregation, but they remain dispersed in the albite-anorthite phase and diffuse the light traversing the crystal, causing it to display colours which vary with the dimensions of the crystallites and their setting with respect to the incident light-beam.

The present paper is concerned with another group of feldspars which give evidence of optical heterogeneity, namely the moonstones. The published analyses show that the potash and soda feldspars are their principal constituents, the former being usually the major and the latter the minor component; a small percentage of lime feldspar is also present. The moonstones enjoy a certain amount of favour as gems by reason of a characteristic optical effect which they display and which is generally known as " schiller ". The investigation described in the paper was undertaken to ascertain the nature and origin of this effect. Though there is an extensive literature on moonstones to which both mineralogists and X-ray workers have contributed, the optical phenomena exhibited by them appear to have received comparatively little attention. The need for studying them is obvious. For, any explanation of the schiller effect which is not based on, or confirmed by, the results of such study must necessarily be regarded as dubious.

2. Materials and Methods

Following the visit by one of us to Ceylon in September 1946, some forty specimens of moonstone in the rough were received as a gift from the owner of the formation near Ambalangoda in that island where they were formerly mined. A few cut specimens also accompanied them, of which one was a particularly fine gem exhibiting a blue schiller. The material thus made available to us has been utilized in the present investigation. To supplement the same, some thirty specimens of cut and polished moonstones were purchased from a dealer in Calcutta and added to our collection. It is understood that they were from the same original source at Ambalangoda. The uncut specimens have been useful, since the cleavages characteristic of feldspar which they occasionally exhibit, enable the crystallographic orientation of the specimens to be determined, a very necessary step in the investigations. On the other hand, the rough surfaces which the uncut specimens generally possess and the internal imperfections manifest in some of them are a serious inconvenience. The polished gem stones are much better in this respect, having evidently been prepared from selected material after removal of the defective portions. By immersing the specimens under study in a cell containing liquid benzene which has nearly the same refractive index as the mineral, the disturbing effects due to reflection, refraction and scattering of light at its external surfaces are minimized. The phenomena having their origin in the interior of the specimen and arising from the passage of light through it can then be conveniently studied. Suitable methods have also had to be improvised for holding the specimen inside the liquid and altering its setting with respect to the direction of the incidence of light as required, and also for determining the orientation of the crystal in such setting.

A comparison of the numerous specimens in our collection throws into relief the striking differences in their individual behaviour. A few pieces exhibit a deep blue but comparatively weak schiller. Others show a blue schiller of decidedly greater intensity. The rest show a schiller which in the different specimens passes by insensible gradations from a blue to bluish white and then to a perfect white; the intensity increases *pari-passu* and in some cases is very great. It is remarkable and obviously significant that specimens from the same locality should show such large differences in their optical characters.

3. Nature of the Schiller Effect

It is a characteristic feature of the schiller of moonstones that the phenomenon is best seen at a particular setting of the crystal determined

by the direction in which the light is incident on it and the direction in which it is observed. When either the setting of the crystal or the direction of incidence of the light is altered, the direction in which the schiller is most conspicuous also shifts. The idea generally current that the schiller owes its origin to a lamellar structure of the feldspar in which layers of orthoclase and albite alternate is based on the fact of observation just mentioned. For, such a structure would reflect light traversing the crystal in a direction varying with its angle of incidence on the planes of the lamellæ. Indeed, measurements have been published[2] which claim to find the orientation of the postulated " schiller-planes " within the crystal in this way. It has even been claimed by one author[3] that examination of cleavage flakes of moonstone under low powers of the microscope when illuminated by light from a point source succeeds in revealing indications of a microperthitic or lamellar structure. Actually, however, the microscope does not reveal any noticeable structure in the typical and most interesting cases, namely the moonstones which exhibit a blue schiller. It should be remarked, further, that the coarse structure of which indications are observed under low powers of the microscope in certain other cases is *prima-facie* incapable of giving rise to the optical phenomena under consideration. As already remarked, an explanation of the origin of the schiller to be acceptable should be based on the results of a detailed study of the phenomenon itself. It was with this idea that the present investigation was undertaken and it has revealed many new facts of interest. These will be set out in the proper places, but we shall proceed first to state those of which the significance in relation to the origin of the schiller is most obvious.

The effects observed with moonstones exhibiting a blue schiller are of particular interest, not only because they are the finest gems, but also by reason of the unambiguous manner in which a study of them reveals the real nature of the phenomena under consideration. As with all the moonstones studied, observations show that the schiller has a maximum intensity when viewed in a particular direction, which is related to the direction of incidence of the light in such manner that the two directions—at least roughly—make equal angles with and lie in the same plane as a particular direction within the crystal which we may designate as the schiller-axis. But the schiller can by no means be described as a reflection of light by a plane or planes within the crystal normal to the schiller-axis. Actually, it has the character of a diffusion of light spread out over a wide range of angles. This is directly evident when the light beam traversing the specimen is of sufficient intensity, as the crystal then becomes itself visible in various directions by reason of the light diffused in its interior. For instance, if the

specimen is set so that the light is incident along the schiller-axis, the schiller is of maximum intensity in the direction backwards towards the source. But it has a notable intensity in various adjoining directions, and it can be seen also in the opposite or forward directions, though more faintly. Viewing the schiller in any particular direction and rotating the crystal about a chosen axis, it is found that the intensity falls off quite slowly on either side of the setting at which it is a maximum. The permissible rotation of the specimen before the schiller ceases to be visible naturally depends on the intensity of illumination and the circumstances of observation. But even with a weak illumination, the angular range is so large that the phenomenon can only be described as a diffusion of light within the crystal. The spectral character of the blue schiller exhibited by the finest moonstones is equally revealing. It is a much richer blue than the blue of the first order in the Newtonian sequence: in other words, it does not permit of being explained as an interference colour due to reflection of light by thin films. On the other hand, it matches more or less perfectly with the deep blue colour exhibited in the diffusion of light by particles which are small in size compared with the wave-length of light. As is well known, this blue is due to the predominance of intensity of the shorter wave-lengths in inverse proportion to their fourth power. Spectroscopic study of the blue schiller of moonstones reveals the same predominance of the shorter wave-lengths and thus compels us to assume a physical origin for it of the same general nature.

On a superficial examination, the bluish-white or white schiller exhibited by the majority of moonstones may be mistaken for a reflection of light within the crystal, the direction in which it is most conspicuous altering with the setting of the crystal in a manner suggesting such an explanation. A careful study, however, reveals various features which are inconsistent with such a description. What is actually observed is that the concentration of intensity around a particular direction which is observed even with the specimens exhibiting a blue schiller becomes more accentuated in these cases. This is accompanied by an increase in absolute intensity and a change in spectral character towards a pure white. Nevertheless, the angular spread of the illumination which simulates a reflection in this manner is readily observable and extends over several degrees of arc. Further, it is accompanied by a diffusion of light which covers a still greater range of angles and the spectral character of which approaches more nearly that of the blue schiller. Even the specimens which normally exhibit a perfect white schiller exhibit diffusion of a sky-blue colour when the light enters the crystal along the schiller-axis and the diffusion is viewed perpendicular to it, or *vice-versa*.

It is evident from the foregoing recital of facts that despite the apparent large differences in optical behaviour of the individual specimens, the phenomena they exhibit are essentially all of the same general nature. We may summarise the factual position by the following statements:—

I. *The schiller of moonstones is a phenomenon arising from the diffusion of light within the crystal.*

II. *The diffusion exhibits optical characters analogous to those observed in the scattering of light by small particles.*

III. *The observed facts give no support to the hypothesis of a micro-perthitic or lamellar structure as the cause of the schiller.*

4. Origin of the Diffusion

It is obvious from what has already been stated that the schiller of moonstones is the result of optical heterogeneity in the feldspar. The most natural assumption to make in the circumstances of the case is that the heterogeneity is associated with the known chemical composition of the mineral. Its two principal constituents, namely, the potash and soda feldspars, are similar in their chemical composition, and hence might reasonably be assumed to be capable of mixing with each other in all proportions and forming a homogeneous crystal. Against this, however, must be set the fact that the two components normally crystallise in different forms, potash feldspar or orthoclase as a monoclinic crystal, and soda feldspar or albite as a triclinic crystal. X-ray study shows that though there is a general resemblance between the crystal structures of orthoclase and albite, there are specific differences, the most significant, as indicated by Table I, being the differences in the lattice spacing along the *a*-axis and in the angle α between the *b*- and

Table I

Lattice Constants

	a	*b*	*c*	α	β	γ
Orthoclase ..	8·45	12·90	7·15	90°	116° 3′	90°
Albite ..	8·14	12·86	7·17	94° 3′	116° 29′	88° 9

the *c*-axes. It has been suggested that the factor which determines whether a feldspar crystallises with monoclinic or triclinic symmetry is the size of the ions which enter into the alumino-silicate frame-work of its structure. Since, however, the sodium and potassium ions are both monovalent and since the former are smaller in size, it should clearly be possible for the

former to replace the latter in the framework of the lattice. In other words, we have good reasons for believing that it should be possible for soda and potash feldspars to mix and form single crystals in the ordinary or the macroscopic sense of the term, even when the former component is present in substantial amounts, possibly even as much as one-half of the entire mineral in its molecular proportion. Two questions, however, arise in this connection. Firstly, in what manner are the sodium ions disposed within the lattice, *viz.*, whether they randomly replace the potassium ions or whether they cluster together in groups, thereby causing the soda feldspar to segregate itself locally from the potash feldspar. Secondly, what changes, if any, are produced in the alumino-silicate framework by the replacement and in particular, whether there are any local alterations in crystal structure produced by the clustering together of the sodium ions. We have also to consider the question of the part played by the third component, namely the lime feldspar, in these dispositions.

The questions raised in the foregoing paragraph have an obvious bearing on our present problem. Theory indicates that the distribution of the two component feldspars within the crystal would profoundly influence its optical behaviour. Only in the particular case of a regular or orderly disposition of the sodium and potassium ions would the crystal be truly homogeneous in the optical sense. Even a random disposition of the ions would give rise to an observable diffusion of light. Much more striking, however, would be the consequence of a disposition of the sodium ions in groups or clusters, in other words, of a segregation of the soda feldspar in the form of tiny crystallites dispersed through the rest of the material. The local fluctuations in chemical composition which such clustering would represent and the fluctuations of refractive index consequent thereon would give rise to a strong diffusion of light, its intensity increasing in proportion to the number of such clusters, multiplied by the square of the volume of each cluster, provided that these are of sufficiently small dimensions and that they can be assumed to be randomly distributed in the available space. Granting that the diffusion of light observed in the moonstones arises in this way, we may remark on the analogy between it and the opalescence exhibited by a mixture of two partially miscible liquids, *e.g.*, carbon disulphide and methyl alcohol at temperatures a little higher than that at which the two components begin to separate from each other. The blue colour of the opalescence of such a liquid mixture at the higher temperatures matches perfectly with the blue schiller of the finest moonstones. As the critical solution temperature of the liquid mixture is approached, there is an enormous increase in the intensity of the opalescence and also a distinct change in its

spectral character as the result of the formation of molecular clusters of rapidly increasing size, until finally a white cloud of visible droplets of liquid is released. There is thus an obvious parallelism between these phenomena and the progressive variations of the colour and intensity of the schiller noticed with different specimens in the group of moonstones.

The comparison made above between the schiller of moonstones and the opalescence of liquid mixtures should not, however, lead us to assume that the phenomena are completely similar to each other in their origin and character. So far from this being the case, many important differences between them are to be expected. It may be remarked, in the first place, that in our present problem, the local fluctuations in the composition occupy fixed positions in the lattice and there is also no reason to suppose that these positions would be distributed completely at random. In consequence, there would be specifiable phase relations between the radiations diffused from different volume elements, and this would necessarily influence the observed distribution of intensity in different directions. There is also no reason for assuming that the clusters of sodium ions in the moonstone would be of spherical shape or that they would be randomly orientated. The known character of the alumino-silicate framework of the feldspars and the differences between the crystal structures of orthoclase and albite would lead us to the opposite conclusion, namely, that the soda feldspar when it segregates and forms crystallites would tend to do so in a fashion related to the structure of the crystal. The shape, size and the orientation of the crystallites thus formed would evidently determine the intensity and spectral character of the radiation diffused by them in various directions. Hence, a notable dependance of the observed phenomena on the setting of the moonstone with respect to the direction in which the light is incident and also on the direction in which it is viewed may be expected. There is another and equally important group of differences between the present problem and that of the diffusion of light in liquid mixtures, namely, in the optical properties of the materials under consideration. The feldspars are birefringent crystals. Though their birefringence is small, we are concerned here with the *differences* in the optical polarisabilities of the medium arising from the local fluctuations in its composition, and these differences would be of the same order of magnitude as the birefringence of the feldspar. Hence, it cannot be supposed the effects under study would be of the same character for all directions of the electric vector in the light traversing the crystal. Special effects in respect of the intensity and state of polarisation of the diffused radiation are accordingly also to be expected. Altogether, it is obvious that the optical phenomena exhibited by moonstones would

present a richer and more complex manifold of effects than the diffusion of light in liquid mixtures.

5. Relationship of the Schiller to Crystal Structure

Reference has already been made to the " schiller-axis " in moonstones which has the property that if light traverses the crystal along that direction, the observed schiller has the maximum intensity in the backward direction, *viz.*, towards the light source. The observations made with our specimens seem to show that the schiller axis is not noticeably different in moonstones exhibiting a blue, a bluish-white or white schiller; it is normal to the *b*-axis of the crystal and inclined to the *c*-axis at 81°. In other words, a plate cut perpendicular to the 010 cleavages and having its faces slightly inclined to the 100 planes of the crystal and making an angle of 9° with them would show the schiller most conspicuously when illuminated and viewed normally. The question arises why the diffusion of light in moonstones exhibits the maximum intensity in these circumstances. Closely related to this effect is another phenomenon observed by us which does not appear to have been previously noticed, namely, that the diffusion of light in moonstone is not symmetric about the schiller-axis but alters in intensity and character as the crystal is rotated about that axis, the directions of inicidence and observation remaining the same. So striking is this non-axiality of the diffusion that its results are evident on a simple inspection of the schiller, when a cut stone is held in the hand and viewed by the light from a window, provided the shape of the stone is not such as to obscure or complicate the situation. Figs. 1 and 2 in Plate XV illustrate the effect, the first being a moonstone with a blue schiller and the second one with a white schiller. Both the stones had been fashioned by the lapidary into a flattened spheroidal shape, the figure axis being practically coincident with the schiller-axis, so that when illuminated and viewed from the front, one would have expected the schiller to manifest itself symmetrically about that axis. Actually, however, we see an elliptical patch of light in both cases and when the crystal is rotated, the elliptic patch turns round with it. It was verified that the longer axis of the elliptic patch was in both cases parallel to the *b*-axis of the crystal; this, as already stated, is itself normal to the schiller-axis. The effects observed with the two specimens may be described thus: the schiller has a sensible intensity over a wider range of angles in the plane containing both the *b*-axis and the schiller-axis than in a plane containing the schiller-axis and perpendicular to the *b*-axis. The same effect shows itself in a peculiar way in Fig. 3 in Plate XV which represents a moonstone which had been shaped by the lapidary into an elongated ellipsoid. Its *b*-axis

was inclined to the longer axis of the ellipsoid. As a consequence, the schiller appears bent into a curve having a point of inflection at the middle.

In all the three cases described above, it is the refraction at the curved surfaces fashioned by the lapidary that enables us to observe the diffusion of light in different directions simultaneously. The same effect may be studied in a more precise fashion by immersing the specimen in benzene liquid and by a rotation about a chosen axis finding how slowly (or how rapidly) the intensity of the diffused light falls off. In every case, it is noticed that the fall of intensity is very rapid if the crystal is rotated about its *b*-axis, but relatively much slower if it is rotated, for instance, about the *c*-axis of the crystal.

The explanation of the effects described above, as well as of those already set out in Section 3, is evidently to be found in a consideration of the size, shape and disposition of the crystallites of soda feldspar resulting from its segregation, since they determine the distribution of intensity of the light diffused in various directions. We proceed to consider the nature of such segregation in its relation to the structure of the crystal as a whole. We shall take it for granted that when the soda feldspar segregates, it would tend to maintain the crystal symmetry as well as the orientation of the crystal axes exhibited by the parent mass and thereby to minimise the disturbance to the crystalline order produced by the segregation. Such a result could evidently be obtained in a number of ways. The simplest would be for the soda feldspar to assume monoclinic symmetry with its axes parallel to those of the parent mass. As can be seen from Table I, this would involve only relatively small changes of the angles between the crystal axes from those of a triclinic form. An alternative would be for the soda feldspar, while retaining a triclinic structure, to mimic monoclinic symmetry by internal twinning of the pericline type in which the direction of the *b*-axis remains unaltered. In this way, the mean directions of the *a*- and the *c*-axes for the twin would be nearly the same as for the axes of the entire crystal. It is evident, however, that the latter result would be more perfectly attained, if simultaneously there is a change in the axial angles so that they approximate more closely to the values required for monoclinic symmetry. Which particular procedure is favoured would evidently be determined by the circumstances and especially by the proportion of soda feldspar present. It is not unlikely also that the lime feldspar present may influence the choice between these different alternatives.

It is evident, however, that while there is thus a variety of possibilities for the structure of the segregated soda feldspar, a change in the lattice

spacing *a* must necessarily occur in every case. This is a consequence of the smaller size of the sodium ion, and it is this difference which would determine the form which the crystallites would take. For, in the grouping of the cells containing the sodium ions which results from their coming together, an extension of the groups along the *a*-axis of the lattice would *not* be favoured. The formation of such a chain would disturb or disrupt all the chains of the alumino-silicate frame-work containing potassium ions along the *a*-axis with which it is linked. *Per contra*, a formation would be favoured in which the cells containing the sodium ions link themselves to others of the same kind along the *b*-axis or along the *c*-axis or more generally in the 100 planes of the crystal. The lattice spacing parallel to the *b*-axis differs from that parallel to the *c*-axis, being nearly double of it, and hence there is no reason to anticipate that a grouping of the cells containing the sodium ions along the *b*-axis and along the *c*-axis would be favoured to an equal extent. As the *c*-spacing is smaller, we may reasonably assume that the latter would be the more favoured arrangement. We are thus led to anticipate that the crystallites of the soda feldspar segregating from the potash feldspar would tend to extend themselves principally along the 100 planes of the crystal, and that in this plane an extension along the *c*-axis would be favoured more than one along the *b*-axis.

Optical theory indicates that as the extension of a diffracting particle or group of particles increases in a particular direction or directions, the intensity of the diffracted radiations would tend to concentrate along perpendicular directions. It follows, as a consequence of what has been stated above, that the moonstones would exhibit a schiller-axis perpendicular to the 100 planes of the crystal, in other words, normal to both the *b*- and *c*-axes of the crystal. Further, the diffusion of light would not exhibit a symmetry about the schiller-axis but would extend to larger angles in a plane containing the *b*-axis than in a plane perpendicular to it. It would probably not be a useful proceeding to discuss why the schiller-axis as actually observed is inclined at an angle of 81° to the *c*-axis of the crystal, instead of being perpendicular to it as deduced above. The considerations on which our argument is based are probably not deep enough to explain this small discrepancy between theory and observation. It is gratifying, however, to be able to record a direct observational proof of the explanation given above for the fact that the diffusion of light is not symmetric about the schiller-axis. Examination of several of our specimens discloses that the schiller exhibits distinct evidence of a fibrous structure running parallel to the *c*-axis of the crystal. A photograph showing this is reproduced in Fig. 4, Plate XV.

6. Intensity and Polarisation of the Schiller

Since the diffusion of light in its passage through the crystal is a consequence of the local variations in its refractive indices resulting from the changes of composition, its intensity would depend on the magnitude of these variations. The principal indices of albite are all greater than those of orthoclase, and the published data[4] show that the indices of moonstone are intermediate between them, and increase with the proportion of soda feldspar present. They are, however, in all cases, nearer the values for orthoclase than those for albite. Table II shows the compositions of orthoclase, of a typical moonstone from Ceylon, and of albite, and their respective refractive indices, as well as the differences between them. If we assume that the local variations in composition result in its approaching those of orthoclase and of albite respectively, the refractive indices would increase or decrease by the amounts shown in the table as differences.

Table II

Composition and Refractive Indices

Mineral	K_2O%	Na_2O%	CaO%	μ_g	μ_m	μ_p
Orthoclase ..	15·0	0·9	0·1	1·5245	1·5228	1·5192
			diff.	0·0037	0·0029	0·0024
Moonstone ..	11·0	3·8	0·2	1·5282	1·5257	1·5216
			diff.	0·0110	0·0071	0·0076
Albite ..	0·4	11·4	0·3	1·5392	1·5328	1·5292

The maximum index μ_g of orthoclase determines its optical polarisability in a direction parallel to the *b*-axis of the crystal, while the minimum index μ_p gives it for a direction nearly parallel to the *a*-axis, and the mean index μ_m corresponds to a direction in the 010 planes of the crystal nearly perpendicular to the *a*-axis, and therefore moderately inclined to the *c*-axis. In the case of moonstone, the foregoing statements would still be valid, but in the case of albite which is a triclinic crystal, they would require modification. It is evident, however, from the figures given in the table that the variations of the maximum refractive index μ_g of moonstone, in other words of the optical polarisability along the *b*-axis, resulting from the changes in composition, would be substantially larger than the changes in optical polarisability along the two other principal directions which, as stated above, are nearly parallel and perpendicular to the *a*-axis, respectively. The changes

in optical polarisability in these two other directions resulting from variations of composition would, however, be of the same order of magnitude. The diffusion of light resulting from the variations in refrative index has an intensity proportional to the square of such variations. Theoretical considerations thus lead us to the very interesting result, that the schiller of moonstones should exhibit an easily observable dependance of intensity on the state of polarisation of the light incident on it, being greater when the electric vector is parallel to the *b*-axis of the crystal and less when it is perpendicular to that axis. When the incident light is unpolarised, the same effects would manifest themselves in a different way, the state of polarisation of the diffused light being largely determined by the component parallel to the *b*-axis.

As is well known, the light diffused in an optically isotropic medium exhibiting local variations of refractive index and traversed by an unpolarised beam of light would be plane-polarised in a transverse direction. Since the schiller of moonstones is also a diffusion of light of the same general nature, we should expect it to manifest similar polarisation effects. In observing and interpreting them, it has to be borne in mind that the crystal is itself birefringent. Hence, the radiation diffused in its interior and traversing it before emergence would undergo changes in its state of polarisation which have to be taken into consideration. This is easier when the setting of the crystal with respect to the direction of incidence of the light and the plane in which the diffused radiations are observed are appropriately chosen. As has already been remarked, the state of polarisation of the light diffused within the crystal would be influenced by the direction of the electric vector with respect to the *b*-axis of the crystal. In other words, it would exhibit a dependance on the setting of the crystal very conspicuously. There is still another point which requires to be noted; not merely the principal refractive indices but also the directions of electric vibration which they refer to are different in orthoclase and in albite. It is therefore not to be expected that the diffused radiations would, in general, be perfectly polarised in a transverse direction as in the case of optically isotropic fluctuations of refractive index, even when the setting of the crystal has been appropriately chosen. Finally, we have to remember that the extension in space of the volume elements within the crystal diffusing the light is by no means always negligibly small. In the case of the moonstones exhibiting a white schiller with a large intensity, the diffusing elements are undoubtedly of appreciable size. The state of polarisation of the light diffused by such elements would necessarily be influenced by this fact.

7. Comparison with the Case of Labradorite

The figures given in Table II enable us to appreciate the reason for the observed differences in the optical behaviour of moonstone and of labradorite. The differences in the refractive indices of the mixture of albite and anorthite which principally constitute labradorite and the refractive indices of the orthoclase crystallites which segregate from them are greater than the average of the fluctuations in refractive indices in the case of moonstone by a numerical factor of about 7. The intensity of the light diffused by volume elements of equal size would be therefore some fifty times greater for labradorite than in moonstone. The brilliancy of the effects exhibited by labradorite despite the fact that the orthoclase which segregates in it is relatively small in quantity is thus readily understood. The circumstances in labradorite are clearly also favourable for the segregated crystallites to appear throughout the mass with a tolerable uniformity of size, a condition necessary for the manifestation of vivid colour in the later stages of segregation. On the other hand, in the case of the moonstone, the materials under consideration, *viz.*, the soda and potash feldspars, are present in comparable quantities and are more or less freely miscible with each other. In these circumstances, we may expect the segregated crystallites to vary widely in their sizes. Thus, except in the earliest stages when all the crystallites are small and therefore give a diffusion of a blue colour, a manifestation of vivid colour is not to be expected in the case of moonstones. There is still another striking difference between the two cases which is indicated by theory and confirmed by observation. The intensity of the diffusion in the case of labradorite is sensibly independent of the direction of the electric vector inside the crystal, and the diffused light, in consequence, exhibits a polarisation of the same character as the diffusion in optically isotropic media. As has already been remarked, a different situation is expected and actually found in the case of the moonstones.

8. Polarised Extinction of Light

There is another group of effects observed with moonstones which are of interest and importance for the elucidation of their structure. As we have seen in the foregoing pages, the diffusion of light in its passage through the moonstone is a consequence of the local variations in composition and the variations in refractive index resulting therefrom. Apart from the effects arising in this way, the Ceylon moonstones are transparent monocrystals which do not exhibit any body-colour. Hence, any loss of light which appears in the passage of a light beam through the moonstone may reasonably be attributed to the deviation of the incident energy as diffused

radiation. In other words, the energy appearing as transmitted light is the incident energy less the energy diffused in various directions. It follows that the extinction of light resulting from its passage through the crystal would exhibit various features which are the counterpart of those observed in diffusion. Besides thus representing the integrated effect of the diffusion, the extinction effects usefully supplement the information given by a study of the diffusion phenomena. As examples of the correlations found between diffusion and extinction in our studies may be mentioned the following instances. The moonstones in our collection, though derived from the same source, show a wide divergence in the colour and intensity of the schiller they exhibit. The extinction phenomena likewise show a similar wide range of behaviour. Again, as the angle which the direction of the incident beam makes with the schiller-axis of a moonstone is gradually increased from 0° to 90°, large changes are observed in the angular distribution of the diffused radiation and in its aggregate intensity; the nature of these changes is related to the colour and intensity of the schiller of the specimen under study. The extinction phenomena likewise show remarkable changes when the angle between the direction of the incident light beam and the schiller-axis is altered, these changes altering in character, as we proceed from the moonstones with a blue schiller to those with a bluish-white and a white schiller respectively. The most interesting features of the extinction of light are the colour and the polarisation observed in various circumstances even when the incident light is unpolarised. These features are found to be closely connected with the spectral character and the polarisation exhibited by the diffusion of light and discussed earlier in the paper.

The following further details may be mentioned by way of supplementing the foregoing brief remarks. The moonstones which exhibit a blue schiller when the light is incident along the schiller-axis show a pale yellow colour by transmitted light, evidently the result of greater extinction of the smaller wave-lengths in the incident light. Examination through a polariser shows that this extinction is more marked for a vibration direction along the *b*-axis of the crystal than for a perpendicular direction. This effect is evidently the counterpart of the greater intensity of the schiller for a vibration along the *b*-axis. As the schiller-axis is turned away from coincidence with the incident light beam to a perpendicular direction, the schiller becomes steadily weaker in intensity, and the extinction likewise tends to zero. Moonstones with a strong white schiller show rather different phenomena. When the specimen is held with the schiller-axis parallel to the incident light, the polarisation in the backward direction parallel to the *b*-axis is hardly observable, evidently because the crystal, in that position, throws back nearly all the

light that it receives. The transmitted light is very weak and shows a yellow colour; it is found to be distinctly polarised with the *b*-axis as the direction of smaller intensity. Moonstones with a white schiller also show a remarkable type of polarised extinction when the light traverses them in a direction nearly perpendicular to the schiller axis. Here again, the setting of the *b*-axis of the crystal with respect to the direction of incidence of the light is found notably to influence the completeness of the extinction and the perfection of the polarisation of the weakly transmitted light. The special polarisation effects observed in these circumstances are rather reminescent of those noticed in the light transmitted by a pile of glass plates held obliquely. But the diffusion of a blue colour simultaneously observed in a transverse direction and the dependence of the phenomena on the setting of the *b*-axis with respect to the plane of incidence serve to remind us that the analogy with the behaviour of a pile of glass plates is only superficial.

9. The X-Ray Evidence

The crystal structure of moonstones has been very extensively investigated by X-ray workers. We shall not here attempt anything like a complete review of the literature, but will content ourselves with referring to some of the more important investigations[5,6,7] in the field. It is evident that for a satisfactory correlation of the optical behaviour of a moonstone with the facts revealed by an X-ray examination of its structure, it is necessary that the same specimens should be studied by both methods, and that the optical evidence should be as complete and detailed as the X-ray evidence with which it is sought be compared. It is essential, for instance, to have quantitative data for the intensity and spectral character of the diffused light and their variations with the setting of the crystal and the direction of observation. Only then it would be possible to estimate the size, shape and orientation of the crystallites of the soda-feldspar which diffuse the light, and to find whether the X-ray evidence supports those findings or at least is not in disagreement with them. We may, however, permit ourselves to make a few comments. The X-ray evidence does indeed support the finding that the soda-feldspar in moonstones tends to segregate from the potash feldspar. Particularly significant are the results of a recent investigation reported in a book[8] by Professor Ito in which the Weissenberg X-ray diagrams of a Korean moonstone containing 7·3% of K_2O, 6·9% of Na_2O, and 0·7% CaO are reproduced and discussed. Though the data are not strictly comparable with those of the Ceylon moonstones, they show clearly that segregation of the soda-feldspar occurs in such a manner as to make a near approach to the structure and symmetry of the parent crystal. We may

remark also on the observation by Chao, Smare and Taylor that certain specimens of moonstones show a faint schiller but give no trace of any additional X-ray reflections; there is also an observation of Chao and Taylor that in certain cases, the supplementary X-ray reflections observed are diffuse. Ito has also remarked that in a number of photographs obtained by him, the Weissenberg diagram consists of bands rather than discrete spots. It is obvious that if the segregated crystallites are sufficiently small and numerous, they could give an observable diffusion of light, but that in the X-ray patterns, the reflections given by them would be smeared out just as they would be in the case of very finely divided colloidal particles. Whether this is the explanation of the facts observed, or whether there is actually some indefiniteness in the crystal structure of the segregated soda-feldspar is a matter for further investigation. There is clearly a need for further studies in which the optical and X-ray behaviour of the specimens are examined with equal thoroughness. The position as it stands now may be conservatively stated thus: the X-ray data do not contradict the evidence regarding structure presented in this paper on the basis of their optical behaviour; on the other hand, they support the main conclusions put forward in the paper.*

10. Concluding Remarks

To avoid overloading the present paper, we have had to confine ourselves to a rather terse statement of the experimental facts on the basis of which the explanation of the schiller of monostone given in the paper has been developed. Much other material regarding the angular distribution of the intensity of the diffused light, its spectral character and its state of polarisation in various circumstances was gathered in the course of our studies. Some of this material was of a quantitative character, as for instance, the determination of the state of polarisation of the schiller for various settings of the crystal and for various angles of observation. Other observations, though of a qualitative character, were of scientific significance, as for instance, the fact that a " residual blue " is exhibited by moonstones

* B. V. Thosar (*Phil. Mag.*, October 1945) described some observations on the spectral character, polarisation and intensity of the schiller of moonstone on the basis of which he concluded that the phenomenon is a reflection of light at the twinning planes of a microcline structure which he assumed it to possess. This view is in such complete contradiction with the facts regarding the optical behaviour of moonstone, to say nothing of the X-ray evidence, that we do not propose to traverse it in detail. Thosar's observations lack certain particulars needed to give them scientific significance. But so far as they go, they are fully explicable in the light of the considerations advanced in the present paper.

FIG. 1 FIG. 2

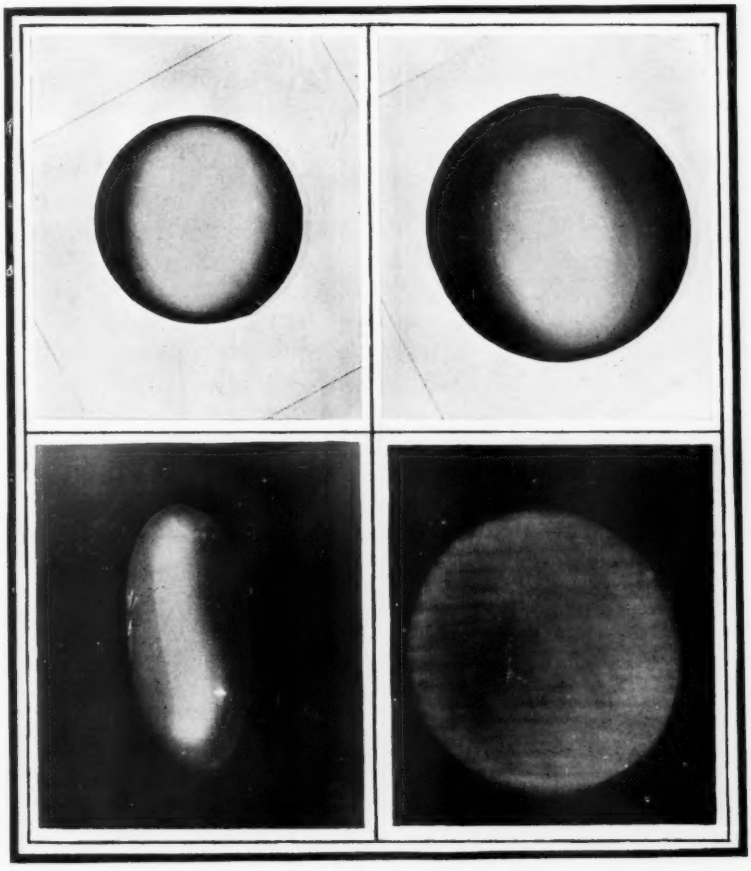

FIG. 3 FIG. 4

giving a white schiller when the latter is extinguished by observation through a polariser. Detailed studies have also been made of the extinction of light in moonstone and of its spectral character and state of polarisation in various circumstances. To have set out all these results in detail here would have diverted attention from the main theme of the paper, namely, the genesis of the schiller as an optical consequence of the local fluctuations in its chemical composition and refractive index. We hope to be able to follow up the present communication by a paper in which the experimental facts of the subject are set out in greater detail.

In conclusion, we have to thank Mr. G. L. Punnyasoma whose generous gift of moonstone specimens from Ambalangoda encouraged us to undertake the present research.

11. Summary

The paper describes the optical behaviour of the moonstones from Ambalangoda in Ceylon which exhibit a wide diversity in the colour and intensity of their schiller. The studies made show that the schiller is a diffusion of light within the material which is macroscopically a monocrystal but exhibits pronounced local variations in its composition and refractive index. Though the potash and soda feldspars mix together when they crystallise, the soda component tends to segregate and form tiny crystallites of which the size, shape and orientation determine the angular distribution of the diffused light, its spectral character, intensity and state of polarisation in various circumstances. The crystallites tend to appear with their greatest extension nearly parallel to the 100 planes of the crystal, the direction of the *c*-axis being preferred more than that of the *b*-axis. The distribution of intensity of the diffused light accordingly does not exhibit a radial symmetry with respect to the direction of its maximum intensity, and this lack of symmetry is conspicuously observable. The intensity of the schiller and its state of polarisation are also markedly influenced by the orientation of the electric vector within the crystal, as a consequence of the variations of refractive index being much greater along the *b*-axis of the crystal than in perpendicular directions. The diffusion of light in moonstone is accompanied by a marked extinction, which exhibits an almost perfect polarisation in certain circumstances. An explanation is given of the striking differences in the optical effects displayed by moonstone and by labradorite in spite of the general similarity in their physical origin.

References

1. C. V. Raman and A. Jayaraman .. *Proc. Ind. Acad. Sci.* A, 1950, **32**, 1.
2. Boggild .. *Math. Fys. Meddl.*. Copenhagen, 1924, **6**, No. 3.
3. Spencer, E. .. *Miner. Mag.*, 1930, **22**, 291.
4. ———— .. *Ibid.*, 1937, **24**, 453.
5. Ito and Inuzuke .. *Z. Kristallogr*, 1936, **95**, 404.
6. Chao, Smare and Taylor .. *Miner. Mag.*, 1939, **25**, 338.
7. —— and Taylor .. *Proc. Roy. Soc.*, 1940, **174**, 57.
8. Tei-Ichi Ito .. *X-Ray Studies on Polymorphism*, Marusen Co., Tokyo, 1950.

THE MEAN SQUARE DEVIATION OF THE NUMBER OF ELECTRONS AND QUANTA IN THE CASCADE THEORY

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1. Introduction

The cascade theory enables one to calculate the mean number of particles to be expected in a shower started by a primary electron or photon of a given energy after a given thickness of material. When one comes to the interpretation of rare cosmic ray events it is also necessary to know something about the fluctuations from this mean in order that one should be able to decide whether an observed shower can be interpreted as a fluctuation, or excluded from this interpretation as being highly improbable. A measure of the fluctuation is provided by the mean square deviation of the number of shower particles in a given energy interval, and the purpose of this paper is to give an explicit formula for this quantity.

Efforts to calculate the fluctuations in cascade showers have been made by several authors, among whom may be named Furry (1937), Euler (1938), Nordsieck, Lamb and Uhlenbeck (1940), and Scott and Uhlenbeck (1942). A lengthy discussion of this problem is to be found in the book of Arley (1943). All the above-mentioned authors except Scott and Uhlenbeck have replaced the actual cosmic-ray problem by a model which corresponds to it to a lesser or greater extent. In some cases one has dealt with a model in which there is only one type of particle having a certain probability of splitting into two per unit distance of travel. In other cases two types of particles, corresponding to the electrons and photons are considered, but the dependence of the radiation and pair-creation processes on the energy of the particles is completely neglected. The only treatment of the problem based on the actual quantum mechanical cross-sections for radiation loss and pair creation has been given by Scott and Uhlenbeck.* The present paper goes further than theirs only in strictly carrying through the calculations to the end. In this way we have calculated and retained certain

* We were unfortunately not aware of the paper by Scott & Uhlenbeck till after our calculations had been completed.

terms which were erroneously omitted by them as being negligible. Explicit expressions for the mean square deviation in the number of particles or quanta in a given energy range are given.

2. Calculation of the Mean Square Deviation

As usual, the cascade problem is treated here as an one-dimensional one and the angular spread of showers is neglected. The thickness of material is measured in the usual units of the cascade theory (*cf.*, for example, Bhabha and Chakrabarty, 1942). The probability of an electron or positron of energy E radiating a quantum of energy $E - E'$ in traversing a unit length in the substance is given by $R(E, E')\,dE'$ while the corresponding probability of a photon of energy E creating a pair of which the electron has an energy between E' and $E' + dE'$ is denoted by $R'(E, E')\,dE'$. Then the mean of the number of particles or photons can be calculated from the functions $n(E; t)$ and $m(E; t)$ respectively† where these functions satisfy the well-known equations of the cascade theory, namely

$$\frac{d}{dt}\,n(E;t) = \int_E^\infty dE' \cdot R(E', E)\,n(E';t) - \int_0^E dE' \cdot R(E, E')\,n(E;t) + 2\int_E^\infty dE' \cdot R'(E', E)\,m(E';t)$$

$$= T_E^{11}\{n(E;t)\} + T_E^{12}\{m(E;t)\} \qquad (1a)$$

$$\frac{d}{dt}\,m(E;t) = \int_E^\infty dE' \cdot R(E', E'-E)\,n(E';t) - \int_0^\infty dE' \cdot R'(E, E')\,m(E;t)$$

$$= T_E^{21}\{n(E;t)\} + T_E^{22}\{m(E;t)\}. \qquad (1b)$$

T_E^{kl} here stand as abbreviations for the four operators which occur in these equations. For example, T_E^{21} acting on any function $f(E)$ of E means

$$T_E^{21}\{f(E)\} = 2\int_E^\infty dE' \cdot R(E', E' - E)\,f(E').$$

† The notation used here is the same as that in a recent paper (Bhabha, 1950) with the difference that the bars over small Roman letters such as n, n_2, nm, etc., have been omitted as being redundant in the present context.

The mean of the number $N(E_1, E_2)$ of particles whose energies lie between E_1 and E_2 is then

$$\overline{N(E_1, E_2)} = \int_{E_1}^{E_2} n(E; t)\, dE. \tag{2}$$

A proper formulation of the stochastic theory of continuous parametric systems has been given recently by one of us (Bhabha, 1950) and it is shown there (Theorem 1) that the mean of the square of $N(E_1, E_2)$ is given by

$$\overline{N(E_1, E_2)^2} = \overline{N(E_1, E_2)} + \int_{E_1}^{E_2}\int_{E_1}^{E_2} n_2(E, E'; t)\, dE\, dE' \tag{3}$$

where the continuous function $n_2(E, E'; t)$ together with the two other function $nm(E, E'; t)$ and $m_2(E, E'; t)$ is determined by the equations‡

$$\begin{aligned}
\frac{d}{dt} n_2(E, E'; t) = &\int_E^\infty d\epsilon \cdot R(\epsilon, E)\, n_2(\epsilon, E') \\
&+ \int_{E'}^\infty d\epsilon \cdot R(\epsilon, E')\, n_2(E, \epsilon) \\
&- \left\{\int_0^E d\epsilon \cdot R(E, \epsilon) + \int_0^{E'} d\epsilon \cdot R(E', \epsilon)\right\} n_2(E, E') \\
&+ 2\int_{E'}^\infty d\epsilon \cdot R'(\epsilon, E')\, nm(E, \epsilon) \\
&+ 2\int_E^\infty d\epsilon \cdot R'(\epsilon, E)\, nm(E', \epsilon) \\
&+ 2m(E + E')\, R'(E + E', E) \\
= &\, T_E^{11}\{n_2(E, E')\} + T_{E'}^{11}\{n_2(E, E')\} + T_E^{12}\{nm(E', E)\} \\
&+ T_{E'}^{12}\{nm(E, E')\} + 2R'(E + E', E)\, m(E + E')
\end{aligned} \tag{4a}$$

‡ For brevity we sometimes omit to write explicitly the dependence of the functions n, n_2, nm etc. on t.

$$\frac{d}{dt}\, nm\,(\mathrm{E}, \mathrm{E}'; t) = \mathrm{T}_{\mathrm{E}}{}^{11}\,\{nm\,(\mathrm{E}, \mathrm{E}')\} + \mathrm{T}_{\mathrm{E}}{}^{12}\,\{m_2\,(\mathrm{E}, \mathrm{E}')\}$$

$$+ \mathrm{T}_{\mathrm{E}'}{}^{21}\,\{n_2\,(\mathrm{E}, \mathrm{E}')\} + \mathrm{T}_{\mathrm{E}'}{}^{22}\,\{nm\,(\mathrm{E}, \mathrm{E}')\}$$

$$+ \mathrm{R}\,(\mathrm{E} + \mathrm{E}', \mathrm{E})\, n\,(\mathrm{E} + \mathrm{E}') \qquad (4b)$$

$$\frac{d}{dt}\, m_2\,(\mathrm{E}, \mathrm{E}'; t) = \mathrm{T}_{\mathrm{E}}{}^{21}\,\{nm\,(\mathrm{E}, \mathrm{E}')\} + \mathrm{T}_{\mathrm{E}'}{}^{21}\,\{nm\,(\mathrm{E}', \mathrm{E})\}$$

$$+ \mathrm{T}_{\mathrm{E}}{}^{22}\,\{m_2\,(\mathrm{E}, \mathrm{E}')\} + \mathrm{T}_{\mathrm{E}'}{}^{22}\,\{m_2\,(\mathrm{E}, \mathrm{E}')\}. \qquad (4c)$$

The last terms in (4*a*) and (4*b*) are responsible for the correlation. In their absence the set of equations (4) would clearly be satisfied by the substitution

$$\begin{aligned} n_2\,(\mathrm{E}, \mathrm{E}') &= n\,(\mathrm{E})\, n\,(\mathrm{E}') \\ nm\,(\mathrm{E}, \mathrm{E}') &= n\,(\mathrm{E})\, m\,(\mathrm{E}') \\ m_2\,(\mathrm{E}, \mathrm{E}') &= m\,(\mathrm{E})\, m\,(\mathrm{E}'). \end{aligned} \qquad (5)$$

We shall solve equations (1) and (4) on the assumption that R and R′ have their respective forms for complete screening, namely

$$\mathrm{R}\,(\mathrm{E}, \mathrm{E}') = \left\{\frac{\mathrm{E}'}{\mathrm{E}} - \left(\frac{4}{3} + \alpha\right)\left(1 - \frac{\mathrm{E}}{\mathrm{E}'}\right)\right\}\frac{1}{\mathrm{E}} \qquad (6a)$$

$$\mathrm{R}'\,(\mathrm{E}, \mathrm{E}') = \left\{1 - \left(\frac{4}{3} + \alpha\right)\left(\frac{\mathrm{E}'}{\mathrm{E}} - \frac{\mathrm{E}'^2}{\mathrm{E}^2}\right)\right\}\frac{1}{\mathrm{E}}, \qquad (6b)$$

α being a small constant (see for example Bhabha and Chakrabarty, 1943). In this case it is convenient to take the Mellin transforms of $n\,(\mathrm{E}; t)$ and $m\,(\mathrm{E}; t)$ thus

$$\nu\,(r; t) = \int_0^\infty \mathrm{E}^{r-1}\, n\,(\mathrm{E}; t)\, d\mathrm{E} \qquad (7a)$$

$$\gamma\,(r; t) = \int_0^\infty \mathrm{E}^{r-1}\, m\,(\mathrm{E}; t)\, d\mathrm{E}. \qquad (7b)$$

Then the functions ν and γ satisfy the equations obtained from (1) by applying the same transformation. Introducing the vector $\phi\,(r; t)$ with two components defined by

$$\underline{\phi}(r;t) = \begin{pmatrix} \nu(r;t) \\ \gamma(r;t) \end{pmatrix} \tag{8}$$

it follows from (1) that ϕ satisfies the matrix equation

$$\frac{d}{dt}\underline{\phi}(r;t) = \underline{\tau}(r)\,\underline{\phi}(r;t) \tag{9}$$

where

$$\underline{\tau}(r) = \begin{pmatrix} -\mathrm{A}_r & \mathrm{B}_r \\ C_r & -\mathrm{D} \end{pmatrix} \tag{10}$$

with the functions A_r to D given by (see for example Bhabha and Chakrabarty, 1943)

$$\mathrm{A}_r = \left(\frac{4}{3} + \alpha\right)\left\{\frac{d}{dr}\log\Gamma(r) + \gamma - 1 + \frac{1}{r}\right\} + \tfrac{1}{2} - \frac{1}{r(r+1)} \tag{11a}$$

$$\mathrm{B}_r = 2\left\{\frac{1}{r} - \left(\frac{4}{3} + \alpha\right)\frac{1}{(r+1)(r+2)}\right\} \tag{11b}$$

$$\mathrm{C}_r = \frac{1}{r+1} + \left(\frac{4}{3} + \alpha\right)\frac{1}{r(r-1)} \tag{11c}$$

$$\mathrm{D} = \frac{7}{9} - \frac{1}{6}\alpha \tag{11d}$$

γ in (11*a*) is the Euler-Mascheroni constant. The matrix $\underline{\tau}$ has the two eigenvalues $-\lambda_r$ and $-\mu_r$ given by

$$\begin{pmatrix} \lambda_r \\ \mu_r \end{pmatrix} = \tfrac{1}{2}(\mathrm{A}_r + \mathrm{D}) \mp \tfrac{1}{2}\{(\mathrm{A}_r - \mathrm{D})^2 + 4\mathrm{B}_r\,\mathrm{C}_r\}^{\frac{1}{2}}. \tag{12}$$

τ can be brought to the diagonal form by the matrix

$$\underline{\sigma}(r) = \begin{pmatrix} \mathrm{D} - \lambda_r & \mu_r - \mathrm{D} \\ \mathrm{C}_r & -\mathrm{C}_r \end{pmatrix} \tag{13}$$

so that defining a matrix

$$\underline{\Lambda}(r;t) = \begin{pmatrix} e^{-\lambda_r t} & 0 \\ 0 & e^{-\mu_r t} \end{pmatrix}. \tag{14}$$

one sees at once that the matrix $\underline{\Sigma}(r;t) = \underline{\sigma}(r)\,\underline{\Lambda}(r;t)$ satisfies

$$\frac{d}{dt}\{\underline{\sigma}(r)\,\underline{\Lambda}(r;t)\} = \underline{\tau}(r)\,\{\underline{\sigma}(r)\,\underline{\Lambda}(r;t)\}. \tag{15}$$

Any solution of (9) is simply obtained by multiplying the matrix $\underline{\sigma\Lambda}$ from the right by a suitable vector. For a shower excited by a single electron of energy E_0, with the boundary condition $n(E;0) = \delta(E - E_0)$, $m(E;0) = 0$ at $t = 0$, or equivalently, $\nu(r;0) = E_0^{r-1}$, $\gamma(r;0) = 0$ at $t = 0$, the solution of (9) is the well-known one

$$\underline{\phi}(r;t) = \underline{\sigma}(r)\,\underline{\Lambda}(r;t)\begin{pmatrix}1\\1\end{pmatrix}\frac{E_0^{r-1}}{\mu_r - \lambda_r}. \tag{16}$$

It follows from (15) that the matrix $\underline{\Sigma}^{-1}(r;t) = \underline{\Lambda}^{-1}(r;t)\,\sigma^{-1}(r)$ satisfies the equation

$$\frac{d}{dt}\,\underline{\Sigma}^{-1}(r;t) = -\,\underline{\Sigma}^{-1}(r;t)\,\underline{\tau}(r) \tag{17}$$

where

$$\underline{\Lambda}^{-1}(r;t) = \begin{pmatrix} e^{\lambda_r t} & 0 \\ 0 & e^{\mu_r t}\end{pmatrix};$$

$$\sigma^{-1}(r) = \frac{1}{(\mu_r - \lambda_r)\,C_r}\begin{pmatrix} C_r & \mu_r - D \\ C_r & -(D - \lambda_r)\end{pmatrix}. \tag{18}$$

To solve the equations (4) we now make a double Mellin Transformion, thus

$$\nu_2(r,s;t) = \int_0^\infty dE \int_0^\infty dE' \cdot E^{r-1}\,E'^{s-1}\,n_2(E,E';t) \tag{19a}$$

$$\nu\gamma(r,s;t) = \int_0^\infty dE \int_0^\infty dE' \cdot E^{r-1}\,E'^{s-1}\,nm(E,E';t) \tag{19b}$$

$$\gamma_2(r,s;t) = \int_0^\infty dE \int_0^\infty dE' \cdot E^{r-1}\,E'^{s-1}\,m_2(E,E';t). \tag{19c}$$

Denoting by $\underline{\phi}^{(2)}(r,s;t)$ the vector

$$\underline{\phi}^{(2)}(r, s; t) = \begin{matrix} \nu_2(r, s; t) \\ \nu\gamma(r, s; t) \\ \nu\gamma(s, r; t) \\ \gamma_2(r, s; t) \end{matrix} \tag{20}$$

and performing a double Mellin transform on the equations (4) one finds without any difficulty that $\phi^{(2)}$ satisfies the equation

$$\frac{d}{dt}\underline{\phi}^{(2)}(r, s; t) = \{\tau(r) \times 1 + 1 \times \tau(s)\}\,\underline{\phi}^{(2)}(r, s; t) + \underline{\psi}(r, s; t) \tag{21}$$

where 1 is the 2×2 unit matrix and ψ is given by

$$\underline{\psi}(r, s; t) = \begin{pmatrix} a_1(r, s)\ \gamma(r+s-1; t) \\ a_2(r, s)\ \nu(r+s-1; t) \\ a_2(s, r)\ \nu(r+s-1; t) \\ 0 \end{pmatrix} \tag{22}$$

and

$$a_1(r, s) = \frac{2\,\Gamma(r)\,\Gamma(s)}{\Gamma(r+s)}\left\{1 - \left(\frac{4}{3} + \alpha\right)\frac{rs}{(r+s+1)(r+s)}\right\} \tag{23a}$$§

$$a_2(r, s) = \frac{\Gamma(r)\,\Gamma(s)}{\Gamma(r+s)}\left\{\frac{s}{r+s} + \left(\frac{4}{3} + \alpha\right)\frac{r}{s-1}\right\}. \tag{23b}$$

The multiplication sign $\times$ in (21) denotes the direct product of two matrices. It follows immediately that in the absence of the $\underline{\psi}$ on the right the solution of (21) would be a direct product of the solutions of (9). Let $\underline{\zeta}(r, s; t)$ be a 4×4 matrix satisfying

$$\frac{d}{dt}\underline{\zeta}(r, s; t) = \{\tau(r) \times 1 + 1 \times \tau(s)\}\,\underline{\zeta}(r, s; t) \tag{24a}$$

so that $\underline{\zeta}^{-1}(r, s; t)$ satisfies

$$\frac{d}{dt}\underline{\zeta}^{-1}(r, s; t) = -\underline{\zeta}^{-1}(r, s; t)\,\{\tau(r) \times 1 + 1 \times \tau(s)\}. \tag{24b}$$

Then a solution of (21) is

$$\underline{\phi}^{(2)}(r, s; t) = \underline{\zeta}(r, s; t)\int_0^t \underline{\zeta}^{-1}(r, s; t)\,\underline{\psi}(r, s; t)\,dt. \tag{25}$$

§ $a_1(r, s)$ is the same as $S(r+1, s-1)$ defined by formula (41*a*) of the paper by Scott and Uhlenbeck. Their (41*a*) is however in error by having $\Gamma(r+s+1)$ in place of $\Gamma(r+s+2)$.

This solution satisfies the boundary condition $\underline{\phi}^{(2)} = 0$ at $t = 0$, corresponding to the fact that at $t = 0$ the shower is initiated by a single electron of energy E_0 only.

It follows from (15) and (24*a*) that

$$\underline{\zeta}(r, s; t) = \{\underline{\sigma}(r) \times \underline{\sigma}(s)\} \{\underline{\Lambda}(r; t) \times \underline{\Lambda}(s; t)\}$$

$$= \underline{\zeta}_0(r, s) \{\underline{\Lambda}(r; t) \times \underline{\Lambda}(s; t)\} \tag{26}$$

where $\underline{\zeta}_0(r, s) = \underline{\sigma}(r) \times \underline{\sigma}(s)$ is given explicitly by (13), and is independent of t. It follows from (13), (14) and (16) that

$$\underline{\psi}(r, s; t) = \underline{\psi}_1(r, s) E_0^{r+s-2} e^{-\lambda_{r+s-1} t} + \underline{\psi}_2(r, s) E_0^{r+s-2} e^{-\mu_{r+s-1} t} \tag{27}$$

where

$$\psi_1(r, s) = \frac{1}{\mu_{r+s-1} - \lambda_{r+s-1}} \begin{pmatrix} a_1(r, s) C_{r+s-1} \\ a_2(r, s) (D - \lambda_{r+s-1}) \\ a_2(s, r) (D - \lambda_{r+s-1}) \\ 0 \end{pmatrix} \tag{28a}$$

$$\underline{\psi}_2(r, s) = \frac{1}{\mu_{r+s-1} - \lambda_{r+s-1}} \begin{pmatrix} - a_1(r, s) C_{r+s-1} \\ a_2(r, s) (\mu_{r+s-1} - D) \\ a_2(s, r) (\mu_{r+s-1} - D) \\ 0 \end{pmatrix}. \tag{28b}$$

Corresponding to the two parts ψ_1 and ψ_2 of ψ, one now finds that $\underline{\phi}^{(2)}$ itself splits into two parts $\underline{\phi}_1^{(2)} + \underline{\phi}_2^{(2)}$. Since the only t dependent factors in the integral in (25) are the exponentials, one finds easily

$$\underline{\phi}_1^{(2)}(r, s; t) = E_0^{r+s-2} \underline{\zeta}_0(r, s) \underline{\eta}(\lambda_{r+s-1}) \underline{\zeta}_0^{-1}(r, s) \underline{\psi}_1(r, s) \tag{29a}$$

and

$$\underline{\phi}_2^{(2)}(r, s; t) = E_0^{r+s-2} \underline{\zeta}_0(r, s) \underline{\eta}(\mu_{r+s-1}) \underline{\zeta}_0^{-1}(r, s) \underline{\psi}_2(r, s) \tag{29b}$$

where $\underline{\eta}(x)$ is the diagonal matrix with the four elements

$$\frac{e^{-xt} - e^{-(\lambda_r + \lambda_s)t}}{\lambda_r + \lambda_s - x}, \quad \frac{e^{-xt} - e^{-(\lambda_r + \mu_s)t}}{\lambda_r + \mu_s - x}, \quad \frac{e^{-xt} - e^{-(\mu_r + \lambda_s)t}}{\mu_r + \lambda_s - x},$$

$$\text{and} \quad \frac{e^{-xt} - e^{-(\mu_r + \mu_s)t}}{\mu_r + \mu_s - x}. \tag{30}$$

Terms of the type $\exp\{-(\lambda_r + \lambda_s)\,t\}$ in (29*a*) can be combined with the corresponding term in (29*b*). We then obtain after some calculation

$$\underline{\phi}^{(2)}(r, s; t) = \underline{\phi}'(r, s; t) + \underline{\phi}_\lambda(r, s; t) + \underline{\phi}_\mu(r, s; t) \tag{31}$$

where

$$\underline{\phi}'(r, s; t) = \mathrm{E}_0^{r+s-2}\,\underline{\zeta}_0(r, s)\,\{\underline{\Lambda}(r; t) \times \underline{\Lambda}(s; t)\}\,\underline{v}'(r, s) \tag{32}$$

$$\underline{\phi}_\lambda(r, s; t) = \mathrm{E}_0^{r+s-2}\,e^{-\lambda_{r+s-1}t}\,\underline{\zeta}_0(r, s)\,\underline{\eta}_0(\lambda_{r+s-1})\,\underline{\zeta}_0^{-1}(r, s)\,\underline{\psi}_1(r, s) \tag{33}$$

$$\underline{\phi}_\mu(r, s; t) = \mathrm{E}_0^{r+s-2}\,e^{-\mu_{r+s-1}t}\,\underline{\zeta}_0(r, s)\,\underline{\eta}_0(\mu_{r+s-1})\,\underline{\zeta}_0^{-1}(r, s)\,\underline{\psi}_2(r, s) \tag{34}$$

the vector v' being given by

$$\underline{v}'(r, s) = \begin{cases} \dfrac{1}{(\lambda_r + \lambda_s - \lambda_{r+s-1})(\lambda_r + \lambda_s - \mu_{r+s-1})}\Big\{(a_1(r, s)\,\mathrm{C}_{r+s-1} \\ \qquad + a_2(r, s)\,\dfrac{\mu_s - \mathrm{D}}{\mathrm{C}_s}(\mathrm{D} - \lambda_r - \lambda_s) + a_2(s, r)\,\dfrac{\mu_r - \mathrm{D}}{\mathrm{C}_r}(\mathrm{D} - \lambda_r - \lambda_s)\Big\} \\ \dfrac{1}{(\lambda_r + \mu_s - \lambda_{r+s-1})(\lambda_r + \mu_s - \mu_{r+s-1})}\Big\{a_1(r, s)\,\mathrm{C}_{r+s-1} \\ \qquad - a_2(r, s)\,\dfrac{\mathrm{D} - \lambda_s}{\mathrm{C}_s}(\mathrm{D} - \lambda_r - \mu_s) + a_2(s, r)\,\dfrac{\mu_r - \mathrm{D}}{\mathrm{C}_r}(\mathrm{D} - \lambda_r - \mu_s)\Big\} \\ \dfrac{1}{(\mu_r + \lambda_s - \lambda_{r+s-1})(\mu_r + \lambda_s - \mu_{r+s-1})}\Big\{a_1(r, s)\,\mathrm{C}_{r+s-1} \\ \qquad + a_2(r, s)\,\dfrac{\mu_s - \mathrm{D}}{\mathrm{C}_s}(\mathrm{D} - \mu_r - \lambda_s) - a_2(s, r)\,\dfrac{\mathrm{D} - \lambda_r}{\mathrm{C}_r}(\mathrm{D} - \mu_r - \lambda_s)\Big\} \\ \dfrac{1}{(\mu_r + \mu_s - \lambda_{r+s-1})(\mu_r + \mu_s - \mu_{r+s-1})}\Big\{a_1(r, s)\,\mathrm{C}_{r+s-1} \\ \qquad - a_2(r, s)\,\dfrac{\mathrm{D} - \lambda_s}{\mathrm{C}_s}(\mathrm{D} - \mu_r - \mu_s) - a_2(s, r)\,\dfrac{\mathrm{D} - \lambda_r}{\mathrm{C}_r}(\mathrm{D} - \mu_r - \mu_s)\Big\} \end{cases} \tag{35}$$

$\underline{\eta}_0(x)$ is just the diagonal matrix obtained from $\underline{\eta}(x)$ by replacing the numerator of every element in the latter by 1.

Denoting the vector in (33), namely $\underline{\zeta}_0(r, s)\,\underline{\eta}_0(\lambda_{r+s-1})\,\underline{\zeta}_0^{-1}(r, s)\,\underline{\psi}_1(r, s)$ by $\underline{v}_\lambda(r, s)$ one finds after a somewhat tedious calculation that its first component is

$$\Big[\{D(D-x)(x_r+x_s)+\lambda_r\mu_r x_s+\lambda_s\mu_s x_r-xx_r x_s\}\, a_1(r,s)\, C_{r+s-1}$$
$$+\frac{(D-\lambda_s)(\mu_s-D)}{C_s}\{D(x_r+x_s)-\lambda_r\mu_r$$
$$+(\lambda_s-x)(\mu_s-x)\}\, a_2(r,s)(D-\lambda_{r+s-1})$$
$$+\frac{(D-\lambda_r)(\mu_r-D)}{C_r}\{D(x_r+x_s)-\lambda_s\mu_s$$
$$+(\lambda_r-x)(\mu_r-x)\}\, a_2(s,r)(D-\lambda_{r+s-1})\Big] \quad (36)$$

$$\{(\mu_{r+s-1}-\lambda_{r+s-1})(\lambda_r+\lambda_s-x)(\lambda_r+\mu_s-x)(\mu_r+\lambda_s-x)$$
$$(\mu_r+\mu_s-x)\}^{-1} \quad (37)$$

where $x=\lambda_{r+s-1}$ and $x_r=\lambda_r+\mu_r-x$. The last component of $\underline{v}_\lambda(r,s)$ is

$$[(C_r C_s(x_r+x_s)\, a_1(r,s)\, C_{r+s-1}+\{A_s(x_r+x_s)-\mu_s\lambda_s$$
$$+(\lambda_r-x)(\mu_r-x)\}\, a_2(r,s)\, C_r(D-\lambda_{r+s-1})$$
$$+\{A_r(x_r+x_s)-\mu_r\lambda_r$$
$$+(\lambda_s-x)(\mu_s-x)\}\, a_2(s,r)\, C_s(D-\lambda_{r+s-1})].$$
$$\{(\mu_{r+s-1}-\lambda_{r+s-1})(\lambda_r+\lambda_s-x)(\lambda_r+\mu_s-x)(\mu_r+\lambda_s-x)$$
$$(\mu_r+\mu_s-x)\}^{-1}. \quad (38)$$

In the paper of Scott and Uhlenbeck the approximation is made of putting all the elements of $\eta_0(x)$ equal to zero except the first element on the diagonal. This is erroneous, since the other elements on the diagonal of $\underline{\eta}_0(x)$ make a contribution to (36) and (38) which is comparable with that of the first diagonal element.

It is clear from (16) and (26) that if $\underline{v}'$ in (32) were replaced by the vector having all its components equal to 1, then the right-hand side of (32) would simply become $\underline{\phi}(r;t)\times\underline{\phi}(s;t)$ a circumstance which would correspond to (5). It is therefore convenient to separate out this part and replace $\underline{v}'(r,s)$ by

$$\underline{v}''(r,s)=\underline{v}'(r,s)-\begin{pmatrix}1\\1\\1\\1\end{pmatrix}. \quad (39)$$

Denoting a vector with the four components $n_2(E, E'; t)$, $nm(E, E'; t)$ $nm(E'; E; t)$, and $m_2(E, E'; t)$ by $f(E, E'; t)$ one obtains through a reversal of the transformation (19)

$$f(E, E'; t) = \frac{1}{(2\pi i)^2} \int_{c-i\alpha}^{c+i\alpha} dr \int_{c-i\alpha}^{c+i\alpha} ds \cdot E^{-r} E'^{-s} \underline{\phi}^{(2)}(r, s; t)$$

$$= f_0(E, E'; t) + f''(E, E'; t) + f_\mu(E, E'; t) + f_\lambda(E, E'; t) \quad (40)$$

c being some positive real number. $f_0(E, E'; t)$ is the vector with the components

$$n(E; t)\, n(E'; t),\ n(E; t)\, m(E'; t),\ n(E'; t)\, m(E, t),$$

$$m(E; t)\ m(E'; t)$$

while

$$f''(E, E'; t) = \frac{1}{(2\pi i)^2} \int \int_{c-i\alpha}^{c+i\alpha} \frac{1}{E_0^2} \left(\frac{E_0}{E}\right)^r \left(\frac{E_0}{E'}\right)^s$$

$$\times \zeta_0(r, s) \{\underline{A}(r; t) \times \underline{A}(s; t)\} \underline{v}''(r, s)\, dr\, ds \quad (41a)$$

$$f_\lambda(E, E'; t) = \frac{1}{(2\pi i)^2} \int \int \frac{1}{E_0^2} \left(\frac{E_0}{E}\right)^r \left(\frac{E_0}{E'}\right)^s e^{-\lambda_{r+s-1} t}$$

$$\times \underline{\zeta}_0(r, s)\, \eta_0(\lambda_{r+s-1})\, \underline{\zeta}_0^{-1}(r, s)\, \underline{\psi}_1(r, s)\, dr\, ds \quad (41b)$$

$$f_\mu(E, E'; t) = \frac{1}{(2\pi i)^2} \int \int \frac{1}{E_0^2} \left(\frac{E_0}{E}\right)^r \left(\frac{E_0}{E'}\right)^s e^{-\mu_{r+s-1} t}$$

$$\times \underline{\zeta}_0(r, s)\, \underline{\eta}_0(\mu_{r+s-1})\, \zeta_0^{-1}(r, s)\, \underline{\psi}_2(r, s)\, dr\, ds. \quad (41c)$$

To get the mean of the square of the number of particles or photons in the energy interval from E_1 to E_2 (3) shows that one has to integrate the f's with respect to E and E' from E_1 to E_2. This simply changes any particular f in (41) to $F(E_1, E_1) + F(E_2, E_2) - 2F(E_1, E_2)$ where $F(E_1, E_2)$ is obtained from the corresponding f in (41) by replacing $E_0^{-2} (E_0/E)^r (E_0/E')^s$ in the integrand by

$$\frac{1}{r-1} \cdot \frac{1}{s-1} \cdot \left(\frac{E_0}{E}\right)^{r-1} \left(\frac{E_0}{E'}\right)^{s-1}.$$

Thus it follows from (3) that

$$\overline{N(E_1, E_2)^2} - \{\overline{N(E_1, E_2}\}^2 = \overline{N(E_1, E_2)} + [\{\underline{F}''(E_1, E_1) + F''(E_2, E_2) - 2F''(E_1, E_2)\} + \{\underline{F}_\lambda(E_1, E_1) + F_\lambda(E_2, E_2) - 2\underline{F}_\lambda(E_1, E_2)\} + \{\underline{F}_\mu(E_1, E_1) + F_\mu(E_2, E_2) - 2\underline{F}_\mu(E_1, E_2)\}]_1 \quad (42)$$

where the 1 at the end of the square bracket indicates that the first component alone of the vector in the brackets is to be taken. To obtain the mean of the square of the number of photons $M(E_1, E_2)$ in the energy interval from E_1 to E_2 one has a corresponding expression with M replacing N in (42), and a suffix 4 at the end of the square brackets. By letting $E_2 \to \infty$ one gets $N(E_1)$ the total number of particles of energy greater than E_1. In that case, provided $E_1 \ll E_0$, the contribution of the last two F's in each curly bracket in (42) is negligible compared with the first, and one obtains to a good approximation

$$\overline{N(E_1)^2} - \{\overline{N(E_1)}\}^2 = \overline{N(E_1)} + \{\underline{F}''(E_1, E_1) + \underline{F}_\lambda(E_1, E_1) + \underline{F}_\mu(E_1, E_1)\}_1. \quad (43)$$

The double integrals for the f's given by (41), or the corresponding ones for the F's can be evaluated by the saddle point method. It is true as usual that but for small t the contribution of f_μ is negligible compared with that of f'' or f_λ while even in f'' given by (41*a*), the contribution comes from the first element in the matrix $\underline{A}(r; t) \times \underline{A}(s; t)$, namely, $\exp\{-(\lambda_r + \lambda_s)t\}$ which exceeds the others by an order of magnitude for all but small t. Thus, one essentially requires to know only the first component of the vector $\underline{v}''(r, s)$ given by (35).

The circumstance that there is a non-vanishing fourth component to the matrix in (41*a*) and likewise a non-vanishing fourth component of the matrix v_λ given by (38) results in the mean square deviation of the number of quanta in any given energy interval differing from its Poissonion value. This means that there is a correlation between the numbers of quanta in two different energy intervals despite the fact that in the equation (4*c*) for m_2 there is no correlation term on the right.

Summary

On the basis of the quantum mechanical cross-sections for radiation emission by electrons and pair creation by quanta when screening is complete, the fluctuation in the mean number of electrons and photons

in any given energy interval in a cascade is calculated. The expression for the mean square deviation of this number is given explicitly in the form of a double integral which can be evaluated by the saddle point method.

References

Arley, N. .. *Stochastic Processes and Cosmic Radiation, G. E. C. Gads Forlag Copenhagen*, 1943.

Bhabha, H. J., and Chakrabarty, S. K... *Proc. Roy. Soc.*, A, 1942, **181**, 267–303.

Euler, H. .. *Zs. f. Phys.*, 1938, **110**, 450.

Furry, H. .. *Phys. Rev.*, 1937, **52**, 569–81.

Nordsieck, A., Lamb, W. E. and Uhlenbeck, G. E. .. *Physica*, 1940, **7**, 344–60.

Scott, W. T., and Uhlenbeck, G. E. .. *Phys. Rev.*, 1942, **62**, 497–508.

NOTE ON THE COMPLETE STOCHASTIC TREATMENT OF ELECTRON CASCADES

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1. Introduction

It is well known that the cascade theory correctly describes the behaviour of a cascade of electrons and photons in their passage through matter. Denoting* the number of particles (electrons *plus* positrons) whose energies lie between E and E′ by $N(E, E')$, one has so far calculated to varying degrees of accuracy the mean $\overline{N(E, E')}$ of this number after a thickness t of material in a shower started by a primary electron or photon of some given energy E_0. The process is, however, a stochastic one, and this information is therefore far from complete. If one wishes to know something about the probable deviation of the actual number from the mean, one has to calculate $\overline{N(E, E')^2}$. If one wishes to know next whether this deviation is more likely to be in the direction of larger or smaller showers, one has to calculate $\overline{N(E, E')^3}$. Complete information about the stochastic process is only obtained if one knows $\overline{N(E, E')^k}$ where k is any positive integer. It has been shown in a recent paper (Bhabha, 1950, Theorem 2) that for a stochastic assembly of continuous parametric systems of a very general nature, which includes in particular the type of physical system with which one is concerned here,

$$\overline{N(E, E')^k} = \sum_{l=1}^{k} a_{kl}\, N^{(l)}(E, E') \tag{1}$$

where

$$N^{(l)}(E, E') = \int_E^{E'} dE_1 \int_E^{E'} dE_2 \ldots\ldots \int_E^{E'} dE_l \cdot n_l(E_1, E_2, \ldots E_l). \tag{2}$$

$n_l(E_1, \ldots E_l)$ is a symmetric function of the l variables $E_1, \ldots E_l$, which we call the lth order correlation function. The coefficients a_{kl} are numbers which do not depend on the particulars of the physical system.

* Use is made of the same notation as in a recent paper (Bhabha, 1950, referred to here as B). It will be assumed that the contents of that paper are known to the reader.

Denoting by $P(N(E, E'))$ the probability of their being N particles with energies lying in the interval E to E′, we have

$$\overline{N(E, E')^k} = \sum_{N=0}^{\infty} N^k P(N), \tag{3}$$

the inversion of which is

$$P\left(N(E, E')\right) = \sum_{k=1}^{\infty} b_{Nk} \overline{N(E, E')^k}, \tag{4}$$

where the numbers b_{Nk} must clearly be independent of the particular features of the physical problem. Substitution of (1) in (4) therefore leads to

$$P\left(N(E, E')\right) = \sum_{l=1}^{\infty} C_{Nl} N^{(l)}(E, E'). \tag{5}$$

Scott and Uhlenbeck (1942) have shown that*

$$C_{Nl} = \frac{(-1)^{l-N}}{N!\,(l-N)!} \qquad l \geqslant N \tag{6}$$

and zero for $l < N$. Thus, one has complete information about the cascade process as soon as one knows all the functions of the type $n_l(E_1, \ldots E_l)$, $l = 1, 2, \ldots$.

It has already been shown by Scott and Uhlenbeck for the simplified model in which there is only one type of particle with a given probability of splitting into two per given thickness of material traversed that n_l is explicitly expressible in the form of repeated integrals with respect to $n(E)$, where $n(E)\,dE$ is the mean of the number of particles in the interval dE. This makes it likely that for the actual cascade problem involving two different physical entities, the particles and the photons, a similar statement may be true. The purpose of this note is to prove this. The fact that two types of physical entities are involved, however, complicates the problem considerably. Instead of one basic function $n(E)$ one has now four functions $n^1(E)$, $m^1(E)$, $n^2(E)$ and $m^2(E)$ corresponding physically to the mean of the number of electrons and photons in a cascade generated by a single electron or photon of energy E_0. Any correlation function $n_p m_q (E_1, \ldots E_p;\ E_{p+1}, \ldots E_{p+q})$

* This simply follows from the fact that if the number of particles in the interval dE is independent of that in any other interval, then $n_l(E_1, \ldots E_l) = n(E_1) \ldots\ldots n(E_l)$, whence $N^{(l)} = (\bar{N})^l$. But in this case one has the Poisson distribution with $P(N) = e^{-\bar{N}} (\bar{N})^N / N!$ Equating of the two sides of (5) in this case leads to (6).

can be expressed in the form of repeated integrals of these four functions and the functions R and R′ which give the probabilities for radiation emission and pair creation respectively.

2. Calculation of the qth Order Correlation

Denote by $R(E, E')\,dE'$ the probability per unit length that a particle (electron or positron) of energy E emits a photon of energy in the interval between E′ and $E'+dE'$, and by $R'(E, E')\,dE'$, the corresponding probability of a photon of energy E creating a pair whose electron (or positron) has an energy between E′ and $E'+dE'$. For the purpose of this paper it is not necessary to specify R or R′ further, and they may be arbitrary functions of E and E′. Let $T^{11}(E)$ stand for an operator which acting on any function $f(E)$ of E turns it into

$$T^{11}(E)f(E) = \int_E^\infty dE' \cdot R(E', E'-E)f(E') - \int_0^\infty dE' \cdot R(E, E')f(E) + \beta \frac{\partial}{\partial E} f(E). \tag{7a}$$

Similarly, let

$$T^{12}(E)f(E) = 2\int_E^\infty dE' \cdot R'(E', E)f(E') \tag{7b}$$

$$T^{21}(E)f(E) = 2\int_E^\infty dE' \cdot R(E', E)f(E') \tag{7c}$$

$$T^{22}(E)f(E) = -\int_0^E dE' \cdot R'(E, E')f(E) \tag{7d}$$

Then, if $n(E;\ t)$ and $m(E;\ t)$ give respectively the mean number of particles and photons at a depth t of material, these are determined by the well known equations of the cascade theory, namely

$$\frac{d}{dt} n(E;\ t) = T^{11}(E)\, n(E;\ t) + T^{12}(E)\, m(E;\ t) \tag{8a}$$

$$\frac{d}{dt} m(E;\ t) = T^{21}(E)\, n(E;\ t) + T^{22}(E)\, m(E;\ t) \tag{8b}$$

Introducing the vector $v(E;\ t)$ by

$$v(E;\ t) = \begin{pmatrix} n(E;\ t) \\ m(E;\ t) \end{pmatrix} \tag{9}$$

these can be written in the matrix form

$$\frac{d}{dt} v(\mathrm{E};\ t) = \mathcal{J}(\mathrm{E})\, v(\mathrm{E};\ t) \tag{10}$$

where $\mathcal{J}(\mathrm{E})$ is an operator matrix with the elements $\mathrm{T}^{kl}(\mathrm{E})$ given by (7).

The equations (8) have two independent sets of solutions corresponding to showers started respectively by an electron or a photon of some energy E_0. The former, which we denote by $n^1(\mathrm{E}_0 \mid \mathrm{E};\ t)$ and $m^1(\mathrm{E}_0 \mid \mathrm{E};\ t)$ satisfies the boundary condition

$$n^1(\mathrm{E}_0 \mid \mathrm{E};\ 0) = \delta(\mathrm{E} - \mathrm{E}_0);\ m^1(\mathrm{E}_0 \mid \mathrm{E};\ 0) = 0 \tag{11a}$$

at $t = 0$, while the second satisfies

$$n^2(\mathrm{E}_0 \mid \mathrm{E};\ 0) = 0;\ m^2(\mathrm{E}_0 \mid \mathrm{E};\ 0) = \delta(\mathrm{E} - \mathrm{E}_0). \tag{11b}$$

We therefore introduce the 2×2 matrix f defined by

$$f(\mathrm{E}_0 \mid \mathrm{E};\ t) = \begin{pmatrix} n^1(\mathrm{E}_0 \mid \mathrm{E};\ t) & n^2(\mathrm{E}_0 \mid \mathrm{E};\ t) \\ m^1(\mathrm{E}_0 \mid \mathrm{E};\ t) & m^2(\mathrm{E}_0 \mid \mathrm{E};\ t) \end{pmatrix}. \tag{12}$$

The matrix f satisfies (10) and the boundary condition

$$f(\mathrm{E}_0 \mid \mathrm{E};\ 0) = \mathbf{1}\, \delta(\mathrm{E} - \mathrm{E}_0) \tag{13}$$

at $t = 0$, where $\mathbf{1}$ stands for the 2×2 unit matrix.

All the qth order correlation functions, namely $n_q(\mathrm{E}_1, \ldots \mathrm{E}_q)$, $n_{q-1}m(\mathrm{E}_1, \ldots \mathrm{E}_{q-1};\ \mathrm{E}_q)$, $n_{q-2}m_2(\mathrm{E}_1, \ldots \mathrm{E}_{q-2};\ \mathrm{E}_{q-1},\ \mathrm{E}_q)$, ... $m_q(\mathrm{E}_1, \ldots \mathrm{E}_q)$ are determined by a set of simultaneous integro-differential equations which can be deduced from the master equation of the cascade theory given in B. The function $n_p m_{q-p}(\mathrm{E}_1, \ldots \mathrm{E}_p;\ \mathrm{E}_{p+1}, \ldots \mathrm{E}_q)$ is symmetric in its first p variables and likewise symmetric in its last $q - p$ variables but not in the two sets of variables separated by a semi-colon. A permutation of any one of the first p variables with any one of the last $q - p$ therefore gives a different function of the q variables E_1 to E_q. One obtains in this way $q!/\{p!\,(q-p)!\}$ different functions of the type $n_p m_{q-p}$ of E_1 to E_q. The total number of functions which are determined simultaneously by the set of integro-differential equations for the qth order correlation functions is therefore

$$\sum_{p=0}^{q} \frac{q!}{p!(q-p)!} = 2^q.$$

It can be seen without much difficulty that the equations are

$$\frac{d}{dt} n_p m_{q-p}(E_1, \ldots E_p;\ E_{p+1}, \ldots E_q;\ t) = \sum_{k=1}^{p} T^{11}(E_k)\, n_p m_{q-p}(E_1, \ldots E_k, \ldots E_p;\ E_{p+1}, \ldots E_q;\ t)$$

$$+ \sum_{k=1}^{p} T^{12}(E_k)\, n_{p-1} m_{q-p+1}(E_1, \ldots \overset{k}{\ldots} \ldots E_p;\ E_{p+1}, \ldots E_q, E_k;\ t)$$

$$+ \sum_{k=p+1}^{q} T^{21}(E_k)\, n_{p+1} m_{q-p-1}(E_1, \ldots E_p, E_k;\ E_{p+1}, \ldots \overset{k}{\ldots} \ldots E_q;\ t)$$

$$+ \sum_{k=p+1}^{q} T^{22}(E_k)\, n_p\, m_{q-p}(E_1, \ldots E_p;\ E_{p+1}, \ldots E_k, \ldots E_q;\ t)$$

$$+ [\sum_{k=1}^{p} \sum_{l=p+1}^{q} R(E_k + E_l, E_l)\, n_p m_{q-p-1}(E_1, \ldots E_k + E_l, \ldots E_p;\ E_{p+1} \ldots \overset{l}{\ldots} \ldots E_q;\ t)$$

$$+ \sum_{k=1}^{p} \sum_{l=1}^{p} R'(E_k + E_l, E_k)\, n_{p-2} m_{q-p+1}(E_1, \ldots \overset{k}{\ldots} \ldots \overset{l}{\ldots}, \ldots, E_p;\ E_{p+1}, \ldots E_q, E_k + E_l;\ t)]. \qquad (14)$$

This clearly shows that the correlation depends directly on the presence of the terms in square brackets in (14), which determines the qth order correlation functions in terms of the $(q-1)$th order functions. The first term in square brackets gives the correlation due to the fact that through one radiation process one simultaneously changes the energy of an electron and creates a photon. The second term in square brackets gives the correlation due to the fact that in one single process a photon disappears simultaneously creating an electron and a positron.

Let $v^{(1)}(E;\ t), v^{(2)}(E;\ t), \ldots v^{(q)}(E;\ t)$ be q different solutions of equation (10). Denote the two components of $v^{(k)}$ by $n^{(k)}(E;\ t)$ and $m^{(k)}(E;\ t)$. Then the vector

$$v^{(1)}(E_1;\ t) \times v^{(2)}(E_2;\ t) \times \ldots \times v^{(q)}(E_q;\ t) \qquad (15)$$

with 2^q components, of which a typical one is

$$r^{(1)}(E_1;\ t)\, r^{(2)}(E_2;\ t) \ldots r^{(q)}(E_q;\ t), \qquad (16)$$

where r stands for either of the symbols n or m would satisfy equation (14) if the term in square brackets were absent. Consider the component (16) in which p of the r's stand for n while the remaining $q-p$ stand for m. This

component is not symmetric in the p E's corresponding to the p n's nor in the $q-p$ E's corresponding to the $q-p$ m's. The expression (16) therefore does not yield an expression for the functions $n_p m_{q-p}$ ($E_1, \ldots E_p$; $E_{p+1}, \ldots E_q$; t) which is always symmetric in the first p E's and in the last $q-p$ E's. An expression for $n_p m_{q-p}$ having the necessary symmetry properties is however obtained at once by symmetrizing (15) or (16) with respect to the indices (1), (2),.... that is by summing expressions of the type (15) or (16) over all possible permutations of the indices (1), (2),..... The resulting 2^q functions would have the correct symmetry properties and would satisfy (14) if the terms in square brackets were absent.

Arrange the 2^q correlation functions $n_p m_{q-p}(E_1, \ldots E_q; t)$ of the qth order as the components of a vector $v_q(E_1, \ldots E_q; t)$. It is convenient to arrange these components in an order which would correspond to the decomposition (15) or (16), that is the order which would naturally arise if v_q were a direct product of the q vectors $v^{(k)}$ as in (15). Then (14) can be written in the form

$$\frac{d}{dt} v_q(E_1, \ldots E_q; t) - \mathcal{J}_q(E_1, \ldots E_q)\, v_q(E_1, \ldots E_q; t) = u_q(E_1, \ldots E_q; t) \tag{17}$$

where $\mathcal{J}_q$ stands for the $2^q \times 2^q$ operator matrix

$$\begin{aligned} \mathcal{J}_q(E_1, \ldots E_q) = {} & \mathcal{J}(E_1) \times \mathbf{1} \times \mathbf{1} \times \ldots \times \mathbf{1} \\ & + \mathbf{1} \times \mathcal{J}(E_2) \times \mathbf{1} \times \ldots \times \mathbf{1} \\ \ldots \quad & + \mathbf{1} \times \mathbf{1} \times \mathbf{1} \times \ldots \times \mathcal{J}(E_q) \end{aligned} \tag{18}$$

and $u_q(E_1, \ldots E_q; t)$ stands for the vector with the components given by the term in square brackets in (14). Assuming all the $(q-1)$th order correlation functions to be known, u_q is a known function of the E's, and therefore given the value of v_q at $t = 0$, $v_q(E_1, \ldots E_q; t)$ is uniquely determined by (17).

Introduce the $2^q \times 2^q$ matrix

$$f_q(E_1', \ldots E_q' \mid E_1, \ldots E_q; t) = f(E_1' \mid E_1; t) \times \times f(E_2' \mid E_2; t) \ldots \times f(E_q' \mid E_q; t) \tag{19}$$

where $f(E_k' \mid E_k; t)$ is defined by (12). Then clearly the matrix f_q satisfies (17) with the right-hand side equal to zero. Moreover, on account of

(13), it follows that

$$f_q(E_1', \ldots E_q' \mid E_1, \ldots E_q;\ 0) = \mathbf{1}\,\delta(E_1' - E_1)\ldots\delta(E_q' - E_q) \quad (20)$$

where $\mathbf{1}$ stands for the $2^q \times 2^q$ unit matrix. The appearance of the δ functions in (20) suggests that it might be more convenient to make use of L. Schwartz's theory of distributions. So far f_q is only defined for $t \geqslant 0$. We now introduce the distribution f_q^{D} throughout the whole $q+1$ dimensional space of the variables $E_1, \ldots E_q$, t through the definition

$$f_q^{\mathrm{D}}(E_1', \ldots E_q' \mid E_1, \ldots E_q;\ t) = \begin{cases} f_q(E_1', \ldots E_q' \mid E_1, \ldots E_q;\ t) & \text{for } t \geqslant 0 \\ 0 & \text{for } t < 0. \end{cases} \quad (21)$$

Then it follows from (20) that

$$\frac{d}{dt} f_q^{\mathrm{D}}(E_1', \ldots E_q' \mid E_1, \ldots E_q;\ t) = \mathbf{1}\,\delta(t)\,\delta(E_1' - E_1)\ldots\delta(E_q' - E_q) + \begin{cases} \frac{d}{dt} f_q(E'_1, \ldots E'_q \mid E_1, \ldots E_q;\ t) & \text{for } t \geqslant 0 \\ 0 & \text{for } t < 0. \end{cases} \quad (22)$$

Hence, the distribution f_q^{D} satisfies the equation

$$\left\{\frac{d}{dt} - \mathcal{J}_q(E_1, \ldots E_q)\right\} f_q^{\mathrm{D}}(E_1', \ldots E_q' \mid E_1, \ldots E_q;\ t-x) = \mathbf{1} \cdot \delta(t-x)\,\delta(E_1' - E_1)\ldots\delta(E_q' - E_q). \quad (23)$$

The distribution f_q^{D} is therefore the elementary solution of the integro-differential equation (23), and it follows immediately from this that

$$v_q(E_1, \ldots E_q;\ t) = \int_{-\infty}^{\infty} dx \int_0^{\infty} dE_1', \ldots \int_0^{\infty} dE_q'\, f_q^{\mathrm{D}}(E_1', \ldots E_q' \mid E_1, \ldots E_q;\ t-x)\, u_q(E_1', \ldots E_q';\ x)$$

$$= \int_0^t dx \int_{E_1}^{\infty} dE_1' \ldots \int_{E_q}^{\infty} dE_q'\, f(E_1' \mid E_1;\ t-x) \times \ldots \times f(E_q' \mid E_q;\ t-x)\, u_q(E_1', \ldots E_q';\ x). \quad (24)$$

Any given component of u_q has the same symmetry properties as the corresponding component of v_q. In consequence v_q defined by (24) has the correct symmetry properties, as it must have, being the unique solution of (17).

Since $f(E' \mid E; t)$ is known, (24) shows that the correlation coefficients of any order can be obtained by successive integration in terms of those of lower order. Formally, therefore, we have the complete solution of the cascade problem, and it would not be difficult to obtain numerical data with the help of an electronic or differential calculator.

Summary

The present note extends to the actual cascade process a result already established by Scott and Uhlenbeck for a model in which there is only one type of physical entity involved. It is shown that with the sole approximation of neglecting the angular divergence of showers complete information about the stochastic process of cascade generation can be calculated. The qth order correlation functions are expressed as integrals involving the $(q-1)$th order correlation functions and the two independent elementary solutions of the cascade equations (8). The latter are the usual functions giving the mean number of electrons and photons in cascades excited respectively by a single electron or photon of some definite energy. If the latter are known exactly, then all the higher order correlation functions can be calculated by repeated integration. One thus obtains explicit expressions for the mean of the qth power of the number of electrons or photons in some finite energy interval, and from this again, through a use of equation (5), of the probability of finding N particles in this energy interval at a depth t in a cascade started by an electron or photon of some given energy.

References

H. J. Bhabha .. *Proc. Roy. Soc.* A, 1950, in course of publication.

Scott and Uhlenback .. *Phys. Rev.*, 1942, **62**, 497–508.

RANEY NICKEL REDUCTIONS

Part II. Thioindigo, 6:6′-Diethoxythioindigo and Thioindoxyl

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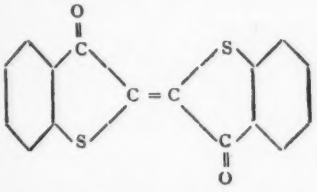
The reactivity of Raney nickel as a reduction catalyst and the desulphurization of sulphur-containing organic compounds by means of Raney nickel have been studied widely in recent years.[1] The removal of sulphur present as part of a ring system has been used in investigating the structure of a few substances, such as β-biotin methyl ester,[2] benzylpenicillin,[3] and the trisulphide from thiobenzophenone.[4] Desulphurization of thiodiphenylamine and benzidinesulphone by Raney nickel[5] and the data on the constitution of the sulphur-containing dyes, Hydron Blue[6] and Cibanone Yellow R,[7] obtained by a study of Raney nickel desulphurization, have been reported by us earlier. The action of Raney nickel and aqueous alkali on thioindigo (Durindone Red B), its 6:6′-diethoxy derivative (Durindone Orange R) and thioindoxyl has now been examined with the result that a new method for the preparation of diphenacyl and its derivatives has become available.

Removal of sulphur from organic compounds by means of Raney nickel at atmospheric pressure is carried out by treatment of the compound (1 part) with a large excess of active Raney nickel[8] (10–30 parts) in a suitable solvent at temperatures up to the boiling point of the solvent.[9] Another method of desulphurization consists in the treatment of the compound (1 part) with Raney (nickel-aluminium) alloy (usually 3 parts) in hot aqueous alkaline solution according to Papa, Schwenk and their collaborators,[10] who have suggested that the reduction is due to the liberation of hydrogen which is then activated by the nickel catalyst. If the nickel catalyst is omitted and the alkaline solution treated with aluminium, no reduction occurs. The mechanism of desulphurization by active Raney nickel, therefore, appears to be the same in both the procedures, but the amount of the catalyst employed when Raney alloy is used is smaller because of the greater availability of the hydrogen produced by the dissolution of aluminium in aqueous alkali.

Desulphurization of thioindigo and its derivatives by means of Raney alloy has been undertaken from two points of view: (1) to use this method for determining the constitution of dyes of the thioindigoid series; and

(2) to synthesize the difficultly accessible diphenacyl and 1 : 4-diphenylbutane derivatives which were expected to be formed by the removal of sulphur from the thioindigoid dyes, followed by reduction of the resulting sulphur-free products. Diphenacyl and its derivatives are not easily accessible and are usually prepared by hydrogenation of the corresponding dibenzoylethylenes.[11] Di- and tetrahydroxy derivatives of diphenacyl have been recently prepared as by-products in the condensation of succinic acid or anhydride with phenol or resorcinol, the major products being the corresponding succineins.[12]

Desulphurization of thioindigo, the parent member of the *bis*-thionaphthene-indigo series of dyes, was first studied. The reduction was carried out by treatment of the dye with varying amounts of Raney alloy in aqueous alkaline solution at about 100°. Reduction of the dye with equal parts of Raney alloy in aqueous alkaline solution gave diphenacyl (I) in about 1·5% yield, together with traces of benzoic acid; and about 50% of the dye was recovered unchanged. The isolation of benzoic acid even under mild conditions of reduction is of interest. When the dye (1 part) was reduced with Raney alloy (4·5 parts), most of the dye was desulphurized, but only a small amount of sulphur-free products could be isolated in the pure state. Thus the yield of pure diphenacyl was only 12%, together with a smaller quantity of benzoic acid. The yield of the sulphur-free products was slightly increased by precipitation of thioindigo from sulphuric acid prior to reduction. Reduction of the dye (1 part) with Raney alloy (6 parts) gave 1 : 4-diphenylbutane (II) as the major product (yield 14%), a small quantity of diphenacyl (about 1%) and benzoic acid (5%). While the formation of diphenacyl and 1 : 4-diphenylbutane was anticipated, the formation of benzoic acid from thioindigo cannot be readily accounted for. The isolation of benzoic acid, together with toluene and *p*-cresol methyl ether, from the Raney nickel reduction products of *p*-methoxybenzyl alcohol has been



Raney alloy, aq·NaOH, 100° →

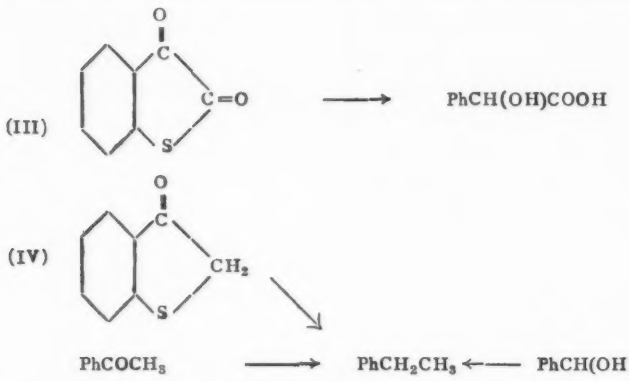
$PhCOCH_2CH_2COPh$ (I)

+ $PhCH_2CH_2CH_2CH_2Ph$ (II

+ $PhCOOH$

recorded; and it has been suggested that benzoic acid is produced by the scheme: dehydrogenation to anisaldehyde → reduction to benzaldehyde → Cannizzaro reaction to benzoic acid and benzyl alcohol (the latter going further to toluene).[10]

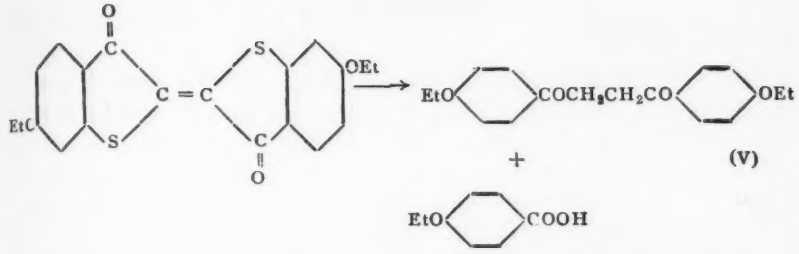
Papa, *et al.*[10] have found that phenyl ketones, PhCOR, are reduced to the corresponding hydrocarbons, $PhCH_2R$, by treatment with Raney alloy in aqueous alkaline solution. They have also recently observed that thioisatin (III) gives mandelic acid, which when treated under similar conditions is unaffected.[10] Blicke and Sheets[13] have recently obtained ethylbenzene from thionaphthene, thioindoxyl (IV), acetophenone and methylphenylcarbinol by treatment with excess of Raney nickel in alcoholic or aqueous sodium carbonate solution. The isolation of compounds in which



a carbonyl group attached to the benzene ring is left unaffected after Raney nickel reduction has, therefore, not been recorded so far. The deactivation of the catalyst by poisoning with the sulphur abstracted from thioindigo may account for diphenacyl, which results by the desulphurization of thioindigo, not undergoing reduction. When, however, excess of Raney alloy was used, diphenacyl (I) was reduced to 1 : 4-diphenylbutane (II).

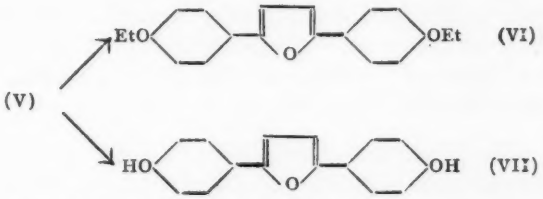
Reduction of thioindoxyl (IV) was then studied, since it forms the intermediate from which thioindigo is prepared by oxidation. When thioindoxyl (1 part) was treated with Raney alloy (4·5 parts) in aqueous alkali, benzoic acid in 8% yield and an oil were obtained. It is interesting to note that acetophenone also gave benzoic acid as one of the reaction products. As stated earlier, the formation of ethylbenzene by Raney nickel desulphurization of thioindoxyl has been observed by Blicke and Sheets;[13] acetophenone is presumably formed as an intermediate product and undergoes further reduction to ethylbenzene.[10]

Desulphurization of 6 : 6′-diethoxythioindigo (Durindone Orange R) was next studied. The dye (1 part), purified by extraction with boiling water and 5% hydrochloric acid, was treated with Raney alloy (4·5 parts)



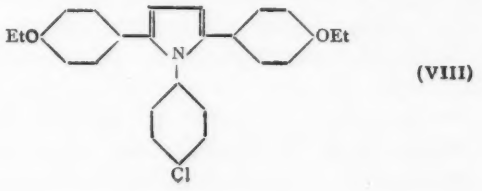
in hot aqueous alkaline solution in the usual manner. Since 50% of the dye was unchanged by this treatment, the purified dye (8 g.) was brought into a finely divided state by dissolving in concentrated sulphuric acid and reprecipitating by drowning in water. When the wet cake was reduced with Raney alloy, reddish orange needles (5·3 g.), m.p. 120–5°, and *p*-ethoxybenzoic acid (0·13 g.) were isolated from the products. The former substance crystallized from alcohol and acetone in pink needles, m.p. 131·5–132°, identical with 4:4′-diethoxydiphenacyl (V), m.p. 132°, prepared by Holleman[14] through a series of reactions starting from phenetole.

Cyclization of (V) by treatment with hydrochloric and acetic acids gave 2:5-*bis*-*p*-ethoxyphenylfuran (VI) in 92% yield. Attempting to deethylate



(V) by heating with pyridine hydrochloride, the product was 2:5-*bis*-*p*-hydroxyphenylfuran (VII) by simultaneous ring closure and deethylation.

Interaction of (V) with excess of *p*-chloraniline in the presence of a little acetic acid (*cf.*, Buu-Hoï[15]) gave the corresponding pyrrole (VIII).



Experimental

Reduction of Thioindigo

Method A.—Durindone Red B 400 pdr. was purified by extraction with boiling water and then with boiling 5% hydrochloric acid, filtered, washed and dried. The purified dye (10 g.) and 10% caustic soda solution (100 c.c.) were mixed in a three-neck flask, fitted with reflux condenser and mercury seal stirrer. The mixture was heated on a water-bath to 90° and Raney alloy (10 g.) was gradually added. After the addition of the alloy, the mixture was further heated on a boiling water-bath for 3 hours under stirring and then filtered. The unreacted dye (4·8 g.) was precipitated by aeration of the filtrate and filtered. The alkaline filtrate was then acidified by pouring into excess of concentrated hydrochloric acid. The acidified solution was ether extracted, and the ether extract after washing, was shaken with 5% sodium bicarbonate solution. The sodium bicarbonate-insoluble substance left after removal of ether was found to contain sulphur and was a sticky solid, which could not be crystallised. The sodium bicarbonate extract was acidified and the small quantity of precipitate which separated was collected and crystallized from water, when it gave colourless needles, m.p. 121°, undepressed when mixed with benzoic acid. The nickel residue was left overnight in dilute hydrochloric acid and then filtered. The filtrate was ether-extracted, when a very small amount of sulphur-containing oil was isolated. The nickel residue was finally extracted with benzene in a Soxhlet. The benzene extract on cooling gave 0·16 g. of the dye, which was separated and the filtrate gave on concentration pale pinkish needles (0·15 g.), m.p. 138–40°, identical with diphenacyl.

Method B.—The purified dye (10 g.) was reduced with Raney alloy (45 g.) in 10% caustic soda solution (450 c.c.) for 6 hours on a water-bath and the reaction mixture was worked up as above. The dye was completely reduced under these conditions. A small quantity of benzoic acid was isolated from the alkaline solution after removal of nickel residue. The nickel residue gave a mixture (3·7 g.) of a crystalline solid and a red oil. The oily portion was readily removed by means of ether. The ether-soluble oil (1·2 g.) which contained sulphur was distilled under vacuum when it gave three liquids having different boiling points. The ether-insoluble crystalline residue gave needles (1·2 g.) from alcohol, m.p. 143–5°, raised to m.p. 144–5° by recrystallization from the same solvent. The elementary analysis and the m.p. show that the reduction product is diphenacyl (Kapf and Paal,[16] m.p. 144–5°) (Found: C, 80·3; H, 5·8. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%). It gave a *bis*-2:4-dinitrophenylhydrazone which crystallized

from acetic acid as a microcrystalline powder, m.p. 264° (decomp.) in agreement with the known diphenacyl-*bis*-2:4-dinitrophenylhydrazone,[17] m.p. 265° (decomp.) (Found: N, 18·6. Calc. for $C_{28}H_{22}N_8O_8$: N, 18·7%). Like diphenacyl, the reduction product gives a green solution in concentrated sulphuric acid which turns red and fluorescent on heating.

Method C.—When the dye (10 g.) was finely divided by precipitation from sulphuric acid and then reduced as above, the desulphurized product was obtained in greater yield (4·5 g.). On macerating the product with ether and removal of the ether-soluble oil, diphenacyl was left as a crystalline residue (1·5 g.).

Method D.—The purified dye (10 g.) was reduced with Raney alloy (60 g.) and 10% caustic soda solution (600 c.c.) for 7 hours on a water-bath. Benzoic acid (0·49 g.) was isolated from the alkaline extract of the reduction mixture. The nickel residue gave a red oil (3·5 g.) which on distillation under reduced pressure yielded two fractions boiling at 160–200°/11 mm. and 260–300°/11 mm. The higher boiling fraction was found to be diphenacyl. The lower boiling fraction (1·32 g.) gave colourless plates from alcohol, m.p. 49–52°, raised to 51·5–52° by recrystallization from the same solvent. The product was finally distilled when a colourless liquid, b.p. 162–5°/13 mm. was obtained, which quickly solidified on cooling to a white solid, m.p. 51·5–52°, found to be identical with 1:4-diphenylbutane (Freund and Immerwahr,[18] m.p. 52°) (Found: C, 91·5; H, 8·5. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%).

Reduction of Thioindoxyl

Thioindoxyl melt (33·4 g.), containing about 30% thioindoxyl, was dissolved in water, acidified and steam distilled. Caustic soda (90 g.) was added to the distillate (900 c.c.) and Raney alloy (45 g.) was added at about 90°. After heating for 3 hours, the reaction mixture was worked up as described earlier. The nickel residue after acidification and ether extraction gave an oil (0·02 g.), which did not yield a 2:4-dinitrophenylhydrazone. The alkaline filtrate was ether extracted, when a red oil was obtained which was not identified. The alkaline solution was then acidified and the product which precipitated (0·8 g.) crystallized from water in colourless needles, m.p. 121°, undepressed when mixed with benzoic acid.

Reduction of acetophenone

Acetophenone (10 g.) was reduced with Raney alloy (30 g.) in 10% caustic soda solution (300 c.c.) for 3 hours on a water-bath. The nickel residue gave a very small yield of an oil which was not examined. The

alkaline filtrate on ether extraction gave an oil (0·2 g.) which distilled between 130–45° (b.p. of ethylbenzene 135°). The alkaline solution on acidification gave a product (0·12 g.) which crystallized from water and was identified as benzoic acid.

Reduction of Durindone Orange R

Durindone Orange R 400 pdr. was purified by successive extraction with boiling water and with boiling 5% hydrochloric acid, and was then employed for reduction.

Method A.—The purified dye (8 g.) was finely divided by precipitation from concentrated sulphuric acid, and the wet cake was treated with Raney alloy (40 g.) in 10% caustic soda solution (400 c.c.) for 1½ hours on a water-bath, when nearly all the dye was found to have decomposed. The mixture was worked up as usual. The dried nickel residue was extracted in a Soxhlet with benzene, and the benzene extract on cooling gave a small quantity (0·07 g.) of the less soluble original dye and a more soluble orange solid (5·3 g., yield 79%), m.p. 120–5°, from the benzene mother-liquor. The orange solid on crystallization from alcohol gave needles (3·2 g.), m.p. 124–7°, which after four recrystallizations from alcohol and two recrystallizations from acetone yielded pale pink needles melting constantly at 131·5–132°. The elementary analysis and the m.p. show that the substance is 4:4′-diethoxydiphenacyl (Holleman,[14] m.p. 132°) (Found: C, 73·9; H, 6·8. Calc. for $C_{20}H_{22}O_4$: C, 73·6; H, 6·8%). The substance gives an intense green solution in concentrated sulphuric acid which quickly changes to deep purple. The purple solution exhibits a deep blue fluorescence. On heating, the colour of the acid solution changes to purple, while heating to the boil gives a pale red solution.

Concentration of the benzene mother-liquor, after separation of 4:4′-diethoxydiphenacyl, gave a small yield of an oil which distills between 240–250°/10 mm. and remains to be identified. The alkaline filtrate, after removal of the nickel residue, did not yield any unreacted dye on aeration. It was then acidified and ether-extracted, and the ether extract shaken with 5% sodium bicarbonate solution. The bicarbonate extract on acidification gave a white solid (0·13 g.), which crystallized from dilute alcohol in colourless needles, m.p. 194–5°, undepressed when mixed with authentic *p*-ethoxybenzoic acid.

Method B.—Reduction of the purified dye (10 g.) with Raney alloy (60 g.) in 10% caustic soda solution (600 c.c.) gave *p*-ethoxybenzoic acid (0·08 g.), 4:4′-diethoxydiphenacyl (3·27 g.) and a red oil which was found to be a mixture of several substances.

2: 5-Bis-p-*ethoxyphenylfuran* (*VI*)

4: 4′-Diethoxydiphenacyl (1 g.) was refluxed with a mixture of glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (16 c.c.) for 10 minutes when a white solid separated. The mixture was diluted with crushed ice (20 g.) and the precipitate collected. The product (0·92 g.), m.p. 166–70°, crystallized from alcohol in colourless, shining plates, m.p. 176–7° raised to 177–177·5°, by recrystallization from the same solvent (Found: C, 77·6; H, 6·4. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5%). The substance gives a greenish blue colour with concentrated sulphuric acid, which changes to a deeper blue on keeping and exhibits a purple colour in transmitted light. On heating, the acid solution changes to red violet. Solutions of the furan in organic solvents show faint violet fluorescence in daylight and more intense violet in ultraviolet light.

2: 5-Bis-p-*hydroxyphenylfuran* (*VII*)

Pyridine hydrochloride (2 g.) and 4: 4′-diethoxydiphenacyl (0·5 g.) were heated at 200–20° for 3½ hours. The mixture was diluted with water and the precipitate which separated was extracted with 5% sodium hydroxide solution. The alkaline extract was acidified and the mixture extracted with ether. The ether extract gave a brown powder (0·38 g.), m.p. 190–200°, which crystallized from dilute alcohol in colourless prismatic needles, m.p. 207–10°, raised to 214–5° by recrystallization from benzene-alcohol (Found: C, 76·0; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). The dihydroxydiphenylfuran gives a red solution in concentrated sulphuric acid, having a bluish violet fluorescence. On heating, the colour of the acid solution changes to deep violet. Solutions of the furan in organic solvents exhibit a pale violet fluorescence in daylight and a more brilliant fluorescence in ultraviolet light.

1-p-*Chlorophenyl*-2: 5-bis-p-*ethoxyphenylpyrrole* (*VIII*)

4: 4′-diethoxydiphenacyl (0·5 g.) and *p*-chloraniline (0·5 g.) were heated with a few drops of acetic acid at 140–60° for one hour. The product, m.p. 80–100°, was extracted with hot water. The water-insoluble portion was dissolved in ether; concentration and cooling gave colourless plates (0·55 g.), m.p. 130–2°, raised to 140–41° by three recrystallizations from *n*-hexane (Found: C, 75·4; H, 6·2; N, 3·2. $C_{26}H_{24}ClNO_2$ requires C, 74·7; H, 5·8; N, 3·4%). The substance gives a red colour in concentrated sulphuric acid, which on slow heating changes to green, blue, brown, violet, and finally brown on boiling. In organic solvents the pyrrole has faint violet fluorescence in daylight, much more intense in ultraviolet light.

Summary

The action of Raney alloy and aqueous alkali on thioindigo, 6:6'-diethoxythioindigo and thioindoxyl has been studied with the result that a new method for the preparation of diphenacyl and its derivatives has become available. Other products which were isolated were benzoic acid and 1:4-diphenylbutane; the latter was formed when excess of Raney alloy was used. 6:6'-Diethoxythioindigo gave 4:4'-diethoxydiphenacyl (V) in 79% yield and *p*-ethoxybenzoic acid. Thioindoxyl and acetophenone on similar treatment also gave benzoic acid.

4:4'-Diethoxydiphenacyl has been converted into 2:5-*bis*-*p*-hydroxyphenylfuran (VII), 2:5-*bis*-*p*-ethoxyphenylfuran (VI) and 1-*p*-chlorophenyl-2:5-*bis*-*p*-ethoxyphenylpyrrole (VIII).

Acknowledgments

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References

1. *Cf.* Baxter and Spring .. *Ann. Rep. Chem. Soc.*, London, 1945, **42**, 100.
   McOmie .. *Ibid.*, 1948, **45**, 199.
2. du Vigneaud, *et al.* .. *J. Biol. Chem.*, 1942, **146**, 475.
3. Cook .. *Quart. Rev. Chem. Soc.*, London, 1948, **2**, 203.
4. Campaigne and Reid .. *J. Org. Chem.*, 1947, **12**, 807.
5. Shah, Tilak and Venkataraman . *Proc. Ind. Acad. Sci.*, 1948, **28 A**, 142.
6. ———— .. *Ibid.*, 111.
7. ———— .. *Ibid.*, 1949, **30 A**, 1.
8. Mozingo .. *Org. Syntheses*, 1941, **21**, 15.
9. ———— *et al.* .. *J. Amer. Chem. Soc.*, 1943, **65**, 1013; 1944, **66**, 1859.
10. Papa, Schwenk, *et al.* .. *J. Org. Chem.*, 1942, **7**, 587; 1944, **9**, 1; 1945, **10**, 232; 1949, **14**, 723; *J. Amer. Chem. Soc.*, 1947, **69**, 3022.
11. Campbell and Khanna .. *J. Chem. Soc.*, 1949, S 33.
12. Seshadri, *et al.* .. *Proc. Ind. Acad. Sci.*, 1947, **26 A**, 299.
13. Blicke and Sheets .. *J. Amer. Chem. Soc.*, 1948, **70**, 3768; 1949, **71**, 4010.
14. Holleman .. *Rec. Trav. Chim.*, 1891, **10**, 220.
15. Buu-Hoï .. *J. Chem. Soc.*, 1949, 2882.
16. Kapf and Paal .. *Ber.*, 1888, **21**, 3056.
17. Heilbron and Bunbury .. *Dictionary of Organic Compounds*, **1**, 1013.
18. Freund and Immerwahr .. *Ber.*, 1890, **23**, 2858.

PHOTO-ELASTICITY OF DIAMOND

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1. Introduction

All the three photo-elastic constants of diamond were first determined by the author (1947) from measurements on the relative and absolute changes of refractive index in specimens subjected to a linear compressive stress. Unfortunately, an error had crept into the measurements whereby the sign of the constants were reversed (West and Makas, 1948; Burstein and Smith, 1948 *b*). It was therefore considered worthwhile to repeat the measurements and obtain fresh values for the piezo- and elasto-optic constants of diamond. The same three specimens of diamond (*viz.*, N.C. 73, N.C. 60 and N.C. 85) from the collection of Sir C. V. Raman, as were used in the original determination, were employed for the present study also. The method used was also essentially the same. It was found that the vertical and horizontal directions had been interchanged by mistake in all the previous measurements. Consequently the piezo-optic constants $(q_{11}-q_{12})$ and q_{44} have nearly the same magnitudes as found earlier, but both are negative and not positive. Further it is found that the individual values of q_{11} and q_{12} have to be revised.

2. Measurements of Relative Retardations

As was mentioned in the earlier paper by the author (1947), measurements made with a Babinet compensator for different directions of compression and observation with three specimens yield the values of three linear functions of $(q_{11}-q_{12})$ and q_{44}, denoted respectively by q_1 and q_3 for brevity. The mean values of these three functions found in the present study are

$$(q_1 + 2q_3)/3 = -4{\cdot}27 \times 10^{-14} \text{ cm.}^2 \text{ dyne}^{-1}$$
$$(q_1 + 5q_3)/6 = -3{\cdot}53 \times 10^{-14} \quad ,,$$
$$q_3 = -2{\cdot}79 \times 10^{-14} \quad ,,$$

The best values of q_1 and q_3 deduced from these are

$$q_1 = -7{\cdot}2 \times 10^{-14},\ q_3 = -2{\cdot}8 \times 10^{-14} \text{ cm.}^2 \text{ dyne}^{-1}$$

Since only $q_1/3$ and $q_1/6$ occur in these functions, it is clear that there is a greater uncertainty in the value of q_1 than in that of q_3. If a crystal could be found with its length along [100] then q_1 can be measured directly.

From the above, the elasto-optic constants are

$$p_{11} - p_{12} = -0{\cdot}40,\ p_{44} = -0{\cdot}12.$$

The above constants are probably correct to 5%.

3. Measurement of Absolute Path Differences

The interference method used earlier was adopted now also, but the fringes obtained with the silvered crystal were not photographed, but were observed directly with a micrometer eye-piece. The diameters of the rings were measured with the eye-piece and in this way a large number of readings could be obtained. The changes in path for the vertically and horizontally polarised rays were obtained by graphical interpolation and found to be $-0{\cdot}053\,\lambda$ and $+0{\cdot}052\,\lambda$ respectively for a load of 5 kg. with the mercury 5461 radiation. The increase in thickness calculated from the elastic constants of Bhagavantam and Bhimasenachar (1946) was 94 Å, so that the changes in path for the two rays were -381 Å and $+193$ Å respectively. The difference is thus 574 Å and as calculated from q_1 and q_3 it is 583 Å, which are in good agreement. These measurements give

$$(q_{11} + q_{12} + q_{44})/2 = -2{\cdot}80 \times 10^{-14}$$

$$(q_{11} + 5q_{12} - q_{44})/6 = +1{\cdot}42 \times 10^{-14}$$

which together with $(q_{11} - q_{12}) = -7{\cdot}2 \times 10^{-14}$

lead to the following values:

$$q_{11} - 5{\cdot}0_5 \times 10^{-14}\ \text{cm.}^2\ \text{dyne}^{-1}$$

$$q_{12} = +2{\cdot}1_5 \times 10^{-14} \quad ,,$$

$$q_{44} = -2{\cdot}8 \times 10^{-14} \quad ,,$$

From these, using the elastic constants, we get

$$p_{11} = -0{\cdot}31,\ p_{12} = +0{\cdot}09,\ p_{44} = -0{\cdot}12$$

The absolute values of q_{11} and q_{12} as also those of p_{11} and p_{12} are expected to be accurate to 10%.

4. Discussion of the Results

The present values differ from those previously reported in that the signs of both $(q_{11} - q_{12})$ and q_{44} and the corresponding elasto-optic constants are negative. This means that diamond behaves as a negative uniaxial crystal for unidirectional pressures along the cubic and octahedral axes and as a negative biaxial crystal for stresses along the [110] or any other direction. It does not however follow that the sign of (dn/dp) is opposite to that reported earlier. This is because the absolute values of p_{11} and p_{12} are different.

Actually it is found that $dn/d\rho$ is negative, since $(p_{11} + 2p_{12})/3 = -0{\cdot}04$ and $\rho dn/d\rho$ has the value $-0{\cdot}28$. Such a negative value for $dn/d\rho$ is to be expected since other highly covalent crystals like MgO (Burstein and Smith, 1948 *a*) have negative $dn/d\rho$. Thus the value of λ in the equation (Mueller, 1935)

$$\rho \frac{dn}{d\rho} = (1 - \lambda) \frac{(n^2 - 1)(n^2 + 2)}{6n}$$

is 1·10, as compared with~ 1·4 for MgO.

R. S. Krishnan (1947), who obtained the Brillouin components in the scattering of light in diamond, found that the relative intensity of the longitudinal and transverse components did not agree with the value calculated from the theory of Leontowitsch and Mandelstamm, (1932) using the author's previously reported photo-elastic constants. This discrepancy, however, disappears with the present data. According to Leontowitsch and Mandelstamm's theory, the average intensities of the longitudinal and transverse components would be in the ratio of

$$\frac{2(p_{12}^2 + p_{44}^2)}{c_{11} + c_{12} + 2c_{44}} : \frac{p_{44}^2}{c_{44}}.$$

With the present values of p_{12} and p_{44} this comes out as 2·04 : 3·35, so that there is no glaring discrepancy between theory and experiments, as was present previously, the transverse component being the brighter of the two.

The author is grateful to Sir C. V. Raman for the loan of the three diamonds used for the study.

Summary

The photo-elastic constants of diamonds have been redetermined and are found to be $q_{11} = -5{\cdot}0_5$, $q_{12} = +2{\cdot}1_5$, $q_{44} = -2{\cdot}8 \times 10^{-14}$ cm.^{2} dyne^{-1} and $p_{11} = -0{\cdot}31$, $p_{12} = +0{\cdot}09$, $p_{44} = -0{\cdot}12$. These lead to a decrease in refractive index when diamond is subjected to a hydrostatic pressure.

References

1. Bhagavantam, S., and Bhimasenachar, J. — *Proc. Roy. Soc.*, 1946, **A, 187**, 381.
2. Burstein, E., and Smith, P. .. *Phys. Rev.*, 1948 *a*, **74**, 229.
   .. *Ibid.*, 1948 *b*, **74**, 1880.
3. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1947, **A, 26**, 411.
4. Leontowitsch, M., and Mandelstamm, S. — *Phys. Z. Sowjet*, 1932, **1**, 317.
5. Mueller, H. .. *Phip. Rev.*, 1935, **47**, 947.
6. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, 1947, **A, 25**, 208.
7. West, C. D., and Makas, A. .. *J. Chem. Phys.*, 1948, **16**, 427.

ALLANITE (MADURA)

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Received August 1, 1950

Occurrence

This rare mineral has been found recently in Sirumalai in the Madura District, Madras Presidency (Sheet 58 F/16). About 40 lbs. of the mineral have been collected. It occurs in a pegmatite band at the southern flank of Kavarkattumalai (long. 77° 56′ 30″ and lat. 10° 16′ 30″). The occurrence is reached by taking a foot-path for a mile up to the base of the hill from the junction of the Puduchatram Road with the Trunk Road between Kodaikanal Road R.S. and Dindigul. This junction is about four miles from Kodaikanal Road Station. The rest of the distance is covered by climbing a height of 1,700 feet from the foot of the hill by a track which ends blindly in the jungle. One has to make one's own way up a steep gradient for the last 100 feet. It was therefore found possible only to take a traverse up to the southern flank of Kavarkattumalai, which is locally known as Kallisholai.

Geological Setting

The Archæan rocks of the region consist of bands of (i) quartz magnetite rocks with magnetite in subordinate quantities; (ii) garnetiferous biotite gneisses with coarse crystals of garnet 1 to 1½ inches across at contacts with quartz veins; (iii) norite and pyroxenite. The bands strike N to NNE-S. to SSW. Quartz veins and dikes and lenses of pegmatites occur as intrusives in the area; the pegmatite dike is nearly a hundred feet thick at Kallisholai. The felspar is flesh-red, reaches a size of one to two cubic feet and decidedly gives a red colour to the pegmatite. Graphic inter-growth with quartz is common. Mica is light green. Allanite is also present.

Mineralogy

The following is a general description of this allanite:

Physical Properties.—Colour: black to velvet black; lustre pitchy with dull black patches; streak brownish grey; fracture subconchoidal to conchoidal; H = 5·5 to 6; G = 3·46.

The mineral fuses easily in the blow pipe flame with intumescence giving a black slag.

Optical Properties.—The refractive index was measured in sodium light by immersion liquids at room temperature 32° C.

Colour: brown showing a net-work of cracks.

Index of refraction: 1·691.

Mostly isotropic under crossed nicols with slightly birefringent grains.

The specific gravity 3·46 which is less than that of commonly described allanite (3·5 to 4·2) is due to hydration. The specific gravity may even reach 2·5 by hydration as reported by Turner.

Chemical Composition

Qualitative chemical tests show that considerable amounts of iron and silica with calcium and cerium are present. Traces of germanium are also noted by spot tests. A quantitative test of some of the constituents is given below:

% Thorium as ThO_2	1·7%
Approximate % rare earths mainly cerium earths	18·0%
Approximate % calcium as CaO	10·5%
Approximate % silica	28·0%
H_2O	1·80%

The physical properties given below, of allanite from Western Australia, agree closely with those of the mineral under study:

Sp. gr.	3·52
n.	1·692

In thin section yellowish-green and isotropic.

The β ray activity indicates 1·35% equivalent uranium content.

A spectrographic analysis of a sample shows that of the rare earths, cerium is present in a major portion with traces of didymium, yttrium and uranium.

H. Winchell who examined the specimen writes that neither this nor any of the known allanites in Yale University collections gave any X-ray pattern.

The mineral occurs in pegmatites in massive to platy forms and in lumps weighing 5 lbs. and more.

ACKNOWLEDGMENTS

The writer is indebted to Professor R. S. Krishnan for the quantitative chemical analysis and determination of the radio-activity content, and to Professor N. R. Tawde, for interpretation of the spectral chart. The courtesy of the Director, King Institute, Guindy, for the use of the spectrograph is thankfully acknowledged.

Since sending the note for publication, Dr. D. N. Wadia who was interested in determining the uranium content, reports that the mineral contains 0·01 p.c. of U_3O_8.

REFERENCES

1. Cooke, S. R. B., and Perry, R. S. .. *Am. Mineral.*, 1945, **30**, 623–28.
2. Dana, E. S. .. *System of Mineralogy*, 6th Edn., Wiley, N. Y., 1914.
3. ——— & Ford, W. E. .. *A Textbook of Mineralogy*, Wiley, N. Y., 1945.
4. Feigl, F. .. *Quantitative analysis by spot tests*, Elsevier Publishing Co., N. Y., 1946.
5. Marble, J. P. .. *Am. Mineral.*, 1940, **25**, 168–73.
6. Richmond, W. E. .. *Ibid.*, 1937, **22**, 290–300.
7. Simson, E. S. .. *Jour. Roy. Soc.*, W. Australia, 1931, **17**, 137–48.
8. Turner, H. W. .. *Econ. Geol.*, 1928, **23**, 62–84.

RAMAN SPECTRUM OF POTASSIUM CHLORATE AND ITS TEMPERATURE VARIATION

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Received June 26, 1950

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

The Raman spectrum of potassium chlorate was first investigated by Krishnamurthy (1930) in the form of crystal powder and later by Venkateswaran (1938) and Hibben (1939). Hibben recorded the maximum number of Raman lines including two low frequency lines. The observed frequency shifts are 125, 179, 478, 493, 620, 915, 930, 975 and 1025 cm.$^{-1}$ From a comparison of the Raman spectrum of potassium chlorate as reported by the earlier workers with that of sodium chlorate (Shanta Kumari, 1948), it is evident that the data on the lattice spectrum of the former are very meagre. Hence it appeared desirable to reinvestigate the Raman spectrum of potassium chlorate using a single crystal. As potassium chlorate is found to be transparent to ultra-violet, the λ 2537 mercury resonance radiation has been used as exciter for this study. The temperature variation of the Raman spectrum is also investigated and the results are presented in this paper.

Specimens of single crystals of potassium chlorate used in the present study were obtained by the method of slow evaporation from aqueous solution of the pure chemical. They were in the form of flat plates of size $10 \times 5 \times 2$ mm., parallel to the c (001) plane. The exciting radiation was incident on the c (001) face of the crystal and the transversely scattered light was taken through the edge. Using a medium quartz spectrograph and a slit-width of 0·025 mm., exposures of the order of two hours were sufficient to get reasonably intense spectrograms. Photographs were taken with exposures of the order of 36 hours but they did not reveal any new features. During long exposures a disturbing effect was noticed, namely, the portion of the crystal facing the intense portion of the arc became frosted due to heating and consequent decomposition in spite of the efficient cooling by fan. Hence, while taking long exposure photographs, fresh crystals were used once every six hours. In replacing the crystals, care was taken to see that the same orientation was adopted.

2. Results

A photograph of the Raman spectrum of potassium chlorate taken at room temperature and its microphotometric record are reproduced in Fig. 1. The positions of the lines are marked in the figure for clarity. The frequency shifts are listed in Table I. The figures given in brackets represent the visual estimate of the relative intensities of the lines. The spectrum recorded by the author exhibits five lines due to the internal oscillations of

Table I

The Raman spectrum of potassium chlorate

Internal oscillations	Lattice oscillations	
$KClO_3$	$KClO_3$	$NaClO_3$
486 (6)	54 (3)	70
620 (1)	82 (3)	83
		103
920 (1)	98 (5)	122·7
930 (10)		131
975 (7)	136 (4) 127	179
	145	

the chlorate ion and five lines due to the lattice oscillations. The appearance of the lines 179, 493 and 1025 cm.$^{-1}$ with zero intensities reported by Hibben could not be confirmed by the author. In the lattice region, four new lines 54, 82, 98 and 145 cm.$^{-1}$ have been recorded. Of these, the doublet 127–45 is broad. The sharp line 82 cm.$^{-1}$ is more clearly seen on the anti-stokes side than on the stokes side. The lines 54 and 620 cm.$^{-1}$ and the doublet nature of the lines 136 and 930 cm.$^{-1}$ were more easily discernible in a lightly exposed picture taken with a finer slit width.

3. Discussion

Potassium chlorate crystallises in the monoclinic prismatic class without water of crystallisation. According to Zachariasen's analysis (1930) of the crystal structure of potassium chlorate, the smallest unit cell contains two molecules of $KClO_3$. The three oxygen atoms are unsymmetrically situated around the chlorine atom forming a distorted ClO_3 group. The correct space group is C^2_{2h}. For this structure, there should be nine lattice oscillations in the Raman spectrum of potassium chlorate as shown below.

T′ and R′ represent respectively the translatory type and rotatory type of lattice oscillations and T represents the translation of the lattice as a

TABLE II

C^2_{2h}	E	C_2	i	σ_h	T	T′	R′	Raman	Infra red
A_1 ..	1	1	1	1	0	4	1	p	f
A_2 ..	1	−1	1	−1	0	2	2	p	/
B_1 ..	1	1	−1	−1	1	1	2	f	p
B_2 ..	1	−1	−1	1	2	2	1	f	p
$U_{R(a)}$ ..	4	0	0	4					
$U_{R(a-v)}$ ..	2	0	0	2					
$h_\rho \chi_\rho'(T)$ ..	3	−1	−3	1					
$h_\rho \chi_\rho'(T')$ ..	9	1	3	3					
$h_\rho \chi_\rho'(R')$ ..	6	0	0	−2					

whole. Of the nine Raman active modes, five come under the symmetric class A_1 and four under class A_2. Again, six should belong to the translatory type and three to the rotatory type. The recorded spectrum of potassium chlorate shows only five lattice lines of which the line 98 cm.$^{-1}$ is most intense. The Raman spectrum of the crystal was photographed for three different orientations of the crystal. The line 98 cm.$^{-1}$ exhibits marked variations in intensity with different orientations and is also found to be highly polarised. This fact suggests that this lattice line should be attributed to the only rotatory oscillation which comes under the symmetric class A_1. The doublet 127–45 cm.$^{-1}$ has a mean value of 136 cm.$^{-1}$ which also coincides with the sum of the other two lattice lines 54 and 82 cm.$^{-1}$ It seems probable that there is only one lattice oscillation with this frequency in the spectrum of potassium chlorate which splits into 127 and 145 cm.$^{-1}$ by Fermi resonance. In Table I are also included the lattice lines of sodium chlorate for comparison. It can be seen that the ratio between the highest frequency shifts in the two cases, namely 136 and 179 cm.$^{-1}$, is inversely proportional to the square root of the mass of the cations. The widths of these two lines are also appreciable. Hence they may be attributed to the mutual oscillations of the chlorate ions against the metallic ions in both cases.

Internal frequencies.—As is well known, the chlorate ion in the free state possesses four fundamental vibrations active in Raman effect, namely 930, 975, 615 and 478 cm.$^{-1}$ with degeneracies 1, 2, 1 and 2 respectively. These four lines are observed in the spectrum of the crystal with nearly the same frequency. It is surprising to note that the doubly degenerate lines

478 and 975 of the free chlorate ion are not split in the spectrum of the crystal in spite of the lower symmetry of the crystal. This suggests that the influence of the potassium ion on the vibrations of the chlorate ion is small in the crystalline state. The line at 930 cm.$^{-1}$ due to the symmetric oscillation, is found to have in the crystal a feeble companion at 920 cm.$^{-1}$ This splitting may be attributed to the fact that there are two molecules in the unit cell.

4. Effect of Temperature

Using the same ultraviolet technique, the Raman spectrum of potassium chlorate was photographed at a series of ten different temperatures, namely, 90, 258, 297, 343, 398, 420, 453, 483, 520, 563 and 603° K. and the variations in the position and width of the prominent Raman lines were studied. With a slit-width of 0·025 mm., exposures of the order of two hours each were given. In order to demonstrate clearly, the effect of temperature on the Raman spectrum, two pictures, one with the crystal held at 603° K. and the other at 90° K. were taken side by side under identical conditions on the same photographic plate using a Hartmann diaphragm. This spectrum is reproduced in Fig. 2. The variations in the position and width of three prominent Raman lines 98, 136 and 975 cm.$^{-1}$ are graphically represented in Figs. 3, 4 and 5. Unlike the case of sodium chlorate (Shanta Kumari, 1950), the symmetric oscillation with frequency shift 930 cm.$^{-1}$ shows a definite shift in position. The line 486 cm.$^{-1}$ does not show any appreciable shift.

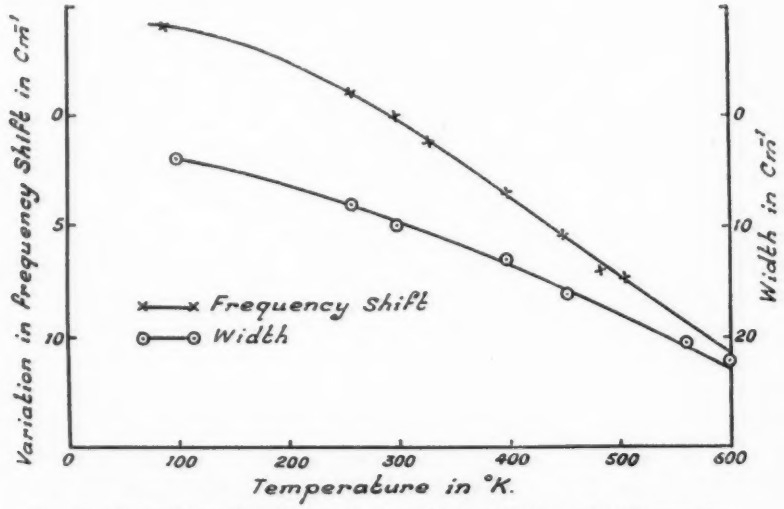

Fig. 3. Temperature dependence of the position and width of 98 Raman line

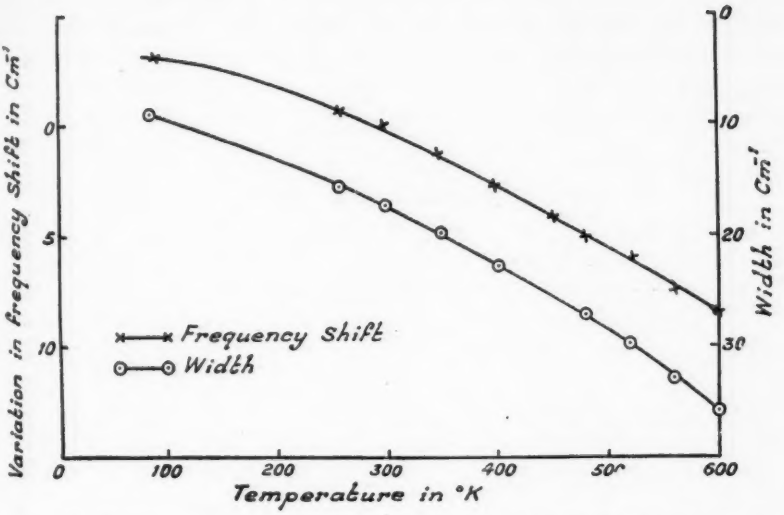

FIG. 4. Temperature dependence of the position and width of 136 Raman line

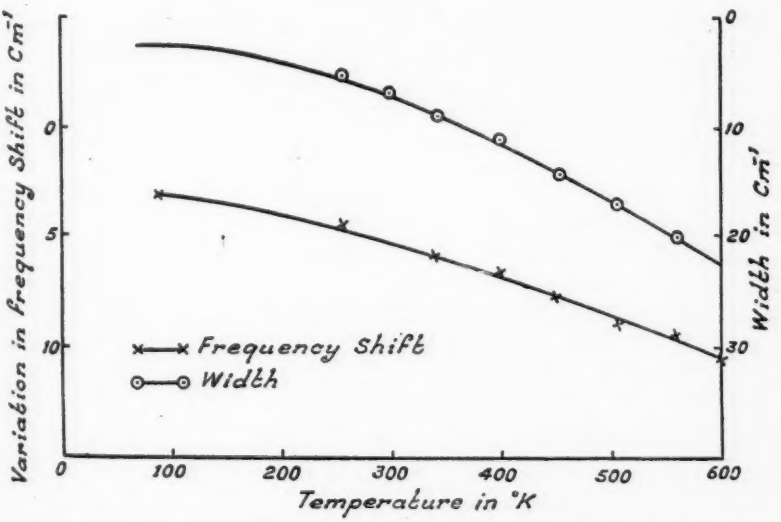

FIG. 5. Temperature dependence of the position and width of 975 Raman line

The total changes in frequency shift and approximate width of these lines together with the proportional change in the two ranges of temperature from 90 to 297° K. and from 297 to 603° K. are entered in Table III.

TABLE III

Total shift and proportional change in the position of Raman lines in potassium chlorate

Raman line cm.$^{-1}$	From 90° to 297° K		From 297° to 603° K		Breadth	
	Shift cm.$^{-1}$	$\chi = -\frac{1}{\nu}\cdot\frac{\partial\nu}{\partial T}$	Shift cm^{-1}	$\chi = -\frac{1}{\nu}\cdot\frac{\partial\nu}{\partial T}$	At 290° K cm.$^{-1}$	At 603° K cm.$^{-1}$
98	4	$197{\cdot}2 \times 10^{-6}$	11	$366{\cdot}8 \times 10^{-6}$	10	22
136	3	$106{\cdot}5 \times 10^{-6}$	8·5	$204{\cdot}3 \times 10^{-6}$	17·2	36
930	1·2	$6{\cdot}27 \times 10^{-6}$	3	$10{\cdot}6 \times 10^{-6}$	12	28
975	2	$5{\cdot}5 \times 10^{-6}$	5·5	$18{\cdot}45 \times 10^{-6}$	7	22

As in the case of other crystals it is found that the proportional change $\chi = -\frac{1}{\nu}\cdot\frac{\partial\nu}{\partial T}$ is different for different Raman lines and for a single Raman line, it is higher at higher temperatures. The graphs show that the variations in frequency shift and width for the individual Raman lines are similar in nature. This suggests that the two effects of temperature, namely, decrease in frequency shift and increase in width of the Raman lines are closely connected to one another as indicated by Sir C. V. Raman (1947).

According to Madan (1886), a change of structure is supposed to take place when potassium chlorate is heated to about 250° C. But Lord Rayleigh (1922) who investigated the optical properties of the crystal at this temperature was of the opinion that the change of structure brought about by heat was macroscopic in character and did not in any way alter the crystal symmetry. In order to settle this issue, the author photographed the Raman spectrum of potassium chlorate with the crystal maintained at the temperatures 225, 247 and 280° C. respectively. The recorded spectra did not indicate any change of crystal structure, thus supporting the conclusions arrived at by Lord Rayleigh.

I wish to place on record my deep indebtedness to Professor R. S. Krishnan for many helpful suggestions and encouragement.

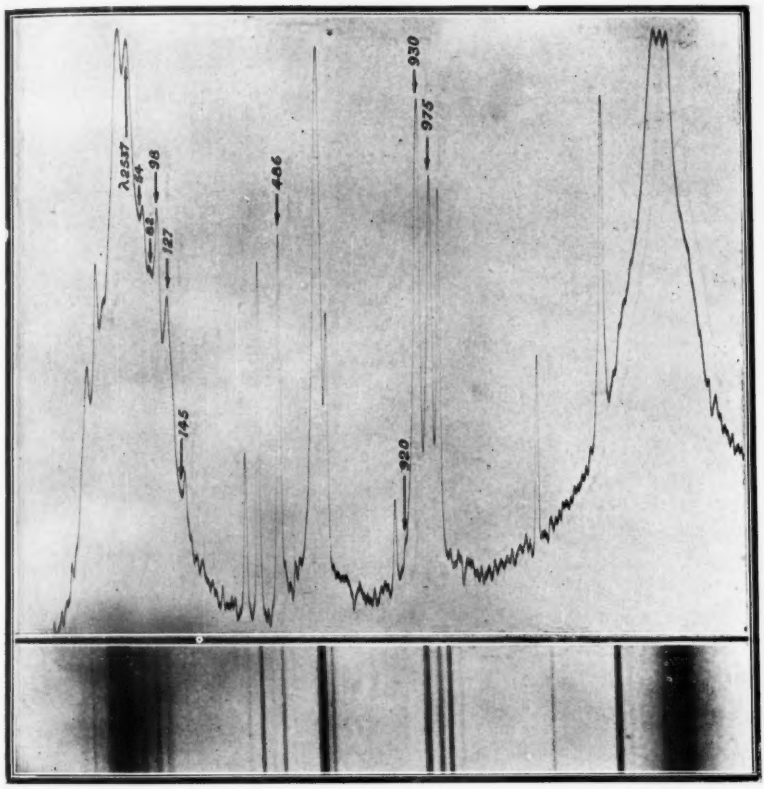

FIG. 1. (*a*) Raman spectrum of Potassium chlorate taken with a medium quartz spectrograph. (*b*) Its microphotometer record.

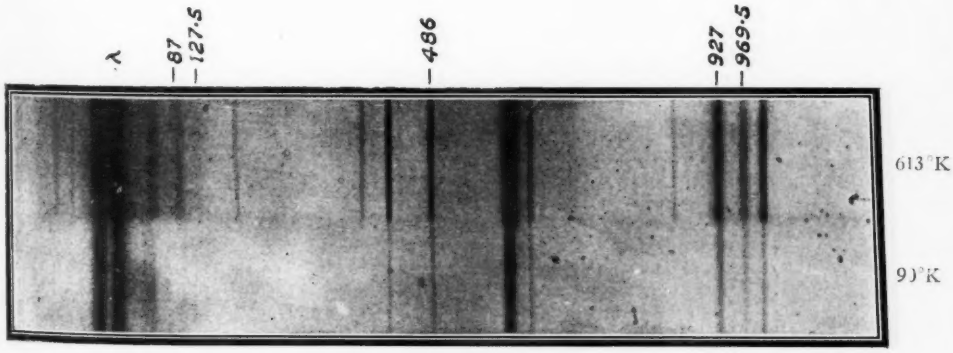

FIG. 2. Raman spectrum of potassium chlorate taken with Hartmann diaphragm

5. Summary

Using the λ 2537 radiation of mercury are as exciter, the Raman spectrum of a single crystal of potassium chlorate has been photographed. The spectrum exhibits 10 Raman lines of which 4 lattice lines 54, 82, 98 and 145 cm.$^{-1}$ have been recorded for the first time.

The variations in the position and width of the prominent Raman lines have been studied at ten different temperatures ranging from 90° to 603° K. The value of the proportional change is found to be different for different Raman lines and is higher at higher temperatures. No change in the crystal symmetry is noticed throughout the temperature range investigated.

References

Hibben .. *Raman Effect and its Chemical Applications*, 1939.

Krishna Murthy .. *Ind. J. Phy.*, 1930, **5**, 633.

Madan .. *Nature*, 1886, **34**, 66.

C. V. Raman .. *Proc. Ind. Acad. Sci.*, 1947, **26**, 511.

Rayleigh .. *Proc. Roy. Soc.*, 1922, **102**, 668.

Shanta Kumari .. *Proc. Ind. Acad. Sci.*, 1948, **28**, 500 ; 1950, **31**, 348.

Venkateswaran .. *Ibid.*, 1938, **7-8**, 144.

Zachariasen .. *Z. f. Krist.*, 1930, **71**, 513.

RAMAN SPECTRA OF CRYSTALLINE TARTRATES

Part IV. Sodium Ammonium Tartrate

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

In continuation of the work on the Raman spectra of crystalline tartrates (Padmanabhan, 1948, 1950), the author has studied for the first time the Raman spectrum of crystalline sodium ammonium tartrate ($NaNH_4C_4H_4O_6$, $4\,H_2O$). The $\lambda\,2537$ radiation of the mercury arc has been employed for excitation.

Single crystals of sodium ammonium tartrate were obtained by the usual process of crystallisation from an aqueous mixture of molar quantities of tartaric acid and sodium carbonate which was neutralised with ammonia. The specimens grown were of small size ($6\times2\times2$ mm.) and the faces were not well developed. Using such small specimens, the spectrograms taken were not as intense as could be desired.

2. Results

In the spectrum of sodium ammonium tartarte thirty-three Raman lines have been identified. Their frequency shifts are entered in Table I.

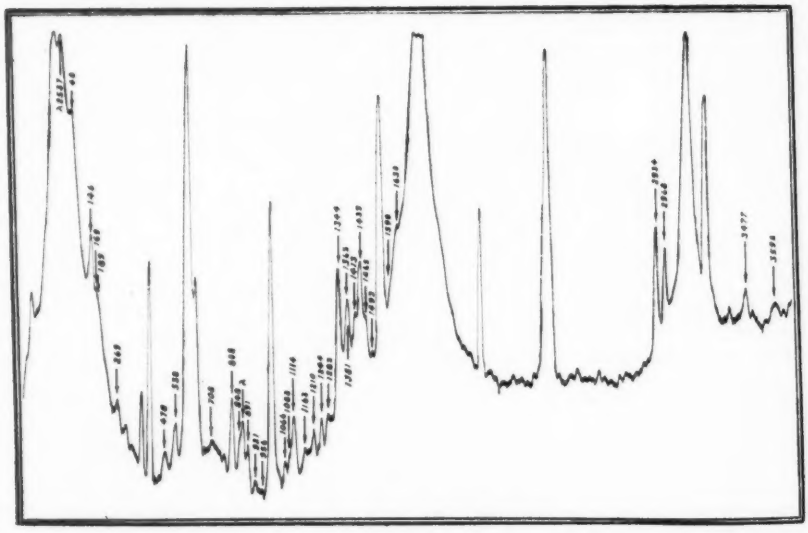

Fig. 2. Microphotometric record of the Raman spectrum of sodium ammonium tartrate

All the Raman lines are marked in the microphotometric record reproduced in Fig. 2, while only the prominent ones are indicated in Fig. 1. The mercury lines are indicated separately by the symbol λ. For purposes of comparison, the values of the frequency shifts of the Raman lines of crystalline sodium tartrate and ammonium tartrate (Padmanabhan, 1948, 1950) are also included in the same table.

TABLE I

Sodium ammonium tartrate	Ammonium tartrate	Sodium tartrate
48	64	42
	78	
	95	83
	115	110
146	136	134
169	168	
189	193	188
215	215 *b*	205
	245	248
269		279
	294	302
	355	353
478		488
538	537 *b*	532
708	703	697
808	805	813
848	840	849
891	901	893
924	920	917
956	988	990
		1037
1086	1073	1072
1114	1103	1112
	1128	
1163	1192	
1210	1215	1209
1244	1265	1247
1282		1287
	1313	
1344	1334	1352
1363	1364	
1381	1388	1381
1413	1407	1404
1439	1445	1432
1465	1468	1463
1493	1493	1496
	1564	1560
1598	1579	1585
	1607	1604
1630		
	2781	
2934	2917	2935
2968	2945	2981
	3022	
	3160	
	3378	3285
	3430	3399
3477		3469
3592		3514

As is to be expected, a close similarity is noticeable between the internal frequencies of the tartrate ion of the three tartrates. The appearance of the two lines due to linear C–H oscillation with different frequency shifts in the three substances (2934 and 2968 in sodium ammonium tartrate, 2917 and 2945 in ammonium tartrate, and 2935 and 2981 in sodium tartrate) suggests that the frequencies due to C–H oscillations are influenced by cation substitution. Unlike the other tartrates, the lattice spectrum of sodium ammonium tartrate contains only a small number of Raman lines, namely four. If one examines the lattice spectra of all the tartrates, two lines stand out very prominently in every one of them. Their frequency shifts are tabulated below:

TABLE II

No.	$(NH_4)_2C_4H_4O_6$	$NaNH_4C_4H_4O_6$ 4 H_2O	$Na_2C_4H_4O_6$ 2 H_2O	$NaKC_4H_4O_6$ 4 H_2O	$K_2C_4H_4O_6$ $\frac{1}{2}$ H_2O
1	64	48	42	38	33
2	136	146	134	132	153

It is interesting to point out that the frequency shift of the first line decreases progressively with increasing atomic weight of the cation indicating thereby that this particular line arises from the oscillations of the cation and anion. The frequencies due to the second line is much less affected by the presence of the cation. This suggests that this line may be due to the oscillations of the tartrate ions in the lattice.

An examination of the spectrum of sodium ammonium tartrate reveals that the only Raman line which could be definitely attributed to the internal oscillations of the NH_4 ion is the one at 1363 cm.$^{-1}$ The other oscillations are evidently too weak to be recorded.

I am grateful to Professor R. S. Krishnan for his suggestions and encouragement.

SUMMARY

Using λ 2537 resonance radiation as exciter, the Raman spectrum of crystalline sodium ammonium tartrate has been recorded for the first time. The spectrum exhibits thirty-three Raman lines. The observed frequency shifts are compared with those of ammonium tartrate and sodium tartrate. The internal frequencies of the NH_4 ion are found to be suppressed in the spectrum of the mixed tartrate.

REFERENCES

Padmanabhan, V. M. .. *Proc. Ind. Acad. Sci.*, 1949, **28**, 485–94.
———— .. *Ibid.*, 1950, **31**, 95–167.

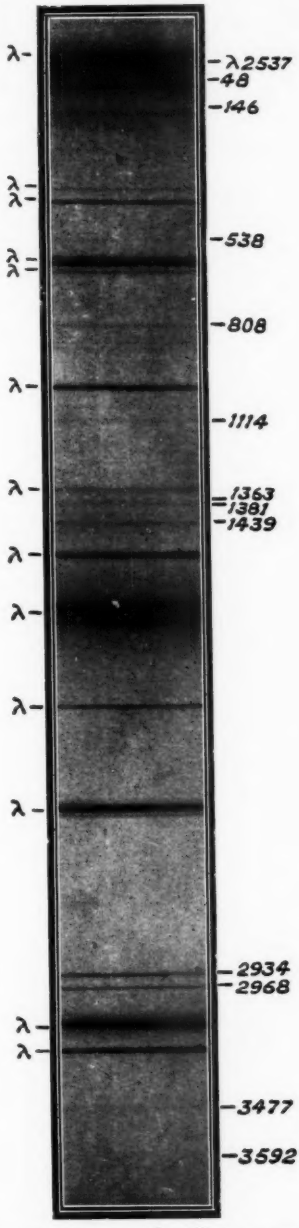

FIG. 1. Raman spectrum of sodium ammonium tartrate

KINETIC STUDIES IN ESTER HYDROLYSIS

Part IV. Alkaline Hydrolysis of Ethyl Acetate in Mixed Solvents*

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Introduction

In the previous part we have presented the results of our investigations on acid hydrolysis of ethyl acetate in dioxan-water and acetone-water systems. The interesting results obtained therein and also the fact that there are still some aspects of the mechanism of the reaction which require elucidation, made it worth while studying alkaline hydrolysis of the ester in the same series of solvent mixtures.

The abstract of a paper by Huang and Hsieh[4] on the saponification of methyl acetate indicated that the reaction rate increased with increasing dioxane content of the solvent and that the rate constant varied linearly with the mole-fraction of dioxane. This evidently means that the reaction velocity is increased by a decrease in dielectric constant. Moelwyn-Hughes[5] has cited this work while dealing with ion-dipole reactions. Glasstone, Laidler and Eyring,[3] on the other hand, have treated alkaline hydrolysis as a reaction between dipoles and have used the results of Fairclough and Hinshelwood[2] on benzoic esters in alcohol-water mixtures to demonstrate the linear variation of log k with $\frac{D-1}{2D+1}$, which is characteristic of dipole-dipole reactions. Reaction velocity is found to be decreased by decrease of dielectric constant. It is easily seen that these two treatments with their respective experimental evidences run counter to each other. This situation calls forth fresh attempts to throw more light on the mechanism of the reaction and the influence of solvent on the reaction rate. In the present study, an effort has been made to vary the dielectric constant over a wide range, but high percentages of organic solvent had to be excluded owing to the limitations imposed by the very low solubility of sodium hydroxide in such media.

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* Part of a thesis of P.M.N. approved for the M.Sc. Degree of the Madras University.

Results and Discussion

A summary of the results obtained are presented in Tables I and II and Figs. 1 and 2 show the variations of k-values with solvent composition.

TABLE I

Second order velocity constants in dioxan-water mixtures

Solvent composition volume % dioxan	Temperature in degrees Centigrade			
	30		40	
	Dielectric constant	$k \times 10^2$	Dielectric constant	$k \times 10^2$
0	(76·8)	16·20	73·12	28·12
10	67·76	16·67	64·49	28·45
20	58·80	12·79	56·84	26·17
30	50·43	11·22	47·05	22·01
40	41·80	10·07	39·54	18·72
50	33·51	8·583	31·66	16·01
60	25·53	7·434	24·11	13·61

TABLE II

Velocity constants in acetone-water mixtures

Solvent composition volume % acetone	Temperature in degrees Centigrade			
	30		40	
	Dielectric constant	$k \times 10^2$	Dielectric constant	$k \times 10^2$
0	(76·8)	16·20	73·12	28·18
10	72·31	15·48	68·95	28·96
20	67·75	13·99	64·60	24·02
30	62·70	11·51	59·80	19·50
40	57·60	9·791	54·99	16·47
50	51·98	7·952	49·62	13·27
70	39·53	6·483	37·69	10·37

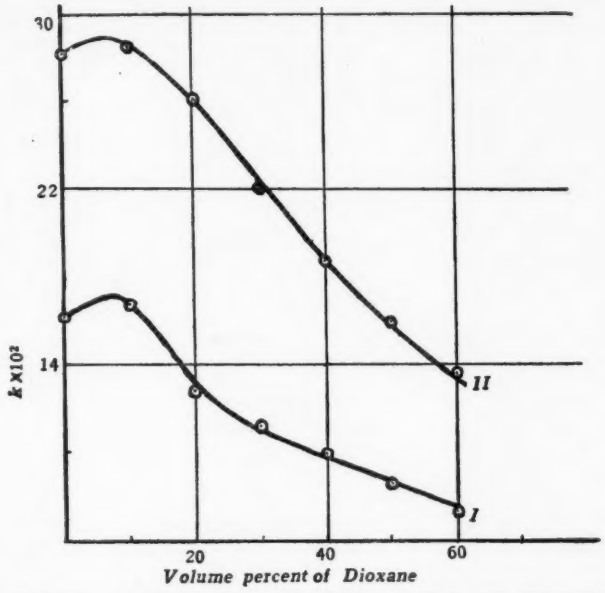

FIG. 1. Variation of velocity with composition I—30° C; II—40° C. (Alk. Hydr.)

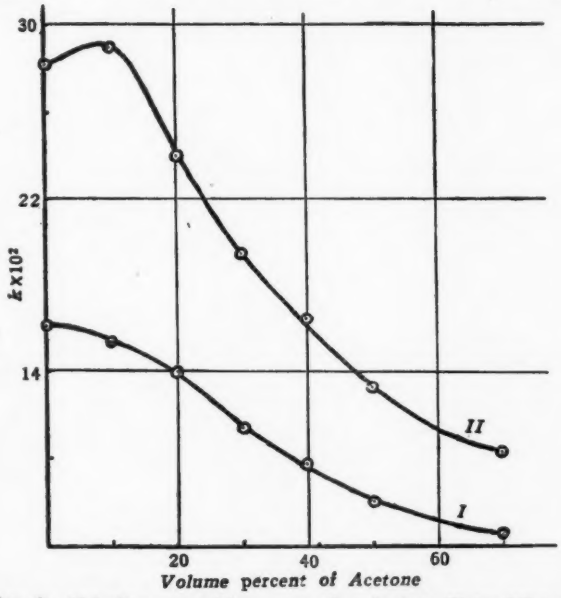

FIG. 2. Velocity composition curves for Acetone-Water Mixtures I—30° C; II—40° C (Alk. Hydr.)

With both solvent mixtures, it is observed that there occurs a maximum in the region of 10% organic solvent excepting in the case of acetone-water mixtures at 30° C. where there is a progressive reduction in reaction rate with increasing amounts of organic solvent. The behaviour here observed in dioxane-water mixtures differs from that found by Huang and Hsieh in the following important respects:—

(i) Instead of a continuous increase with increasing amount of dioxane (*i.e.*, with decreasing dielectric constant), the velocity constant begins to fall when the dioxane content exceeds a certain value. (ii) Also, the composition range over which the velocity increases is found to be much smaller.

The variation observed seems to suggest that the reaction is one between ion and dipole in compositions below 10% and between dipole and dipole for compositions above 10%, if dielectric constant is considered to be the major factor affecting the reaction rate. Since there can be no doubt about the indispensability of the hydroxyl ion for the formation of the transition complex, the remarkable change in trend of the rate constant necessitates a detailed examination of the exact role of the water molecule in alkaline hydrolysis. All aspects of the problem will be more fully considered in Part V.

While recognising the limitations of observations at only two temperatures, it is nonetheless useful to compute the parameters of the arrhenius rate equation. The experimental activation energies and the frequency factors are given in Table III.

TABLE III

Activation energies and frequency factors

Volume % of organic solvent	Dioxane Water		Acetone Water	
	E Kilocals.	Frequency factor Log_{10} PZ	E Kilocals.	Frequency factor Log_{10} PZ
0	10·42	6·73	10·42	6·73
10	13·78	9·08	11·80	7·70
20	13·48	8·83	10·18	6·49
30	12·69	8·21	9·93	6·22
40	12·19	7·79	9·79	6·06
50	11·74	7·41	9·95	5·86
60	11·39	7·09	..	..
70	..	..	8·84	5·19

Excepting for the sharp increase when the solvent composition changes from 0% to 10% organic solvent, variations of both E and PZ values with composition are quite gradual. Fig. 3 shows that unlike in the case of acid hydrolysis the variations in activation energy in the two series of solvents are quite similar.

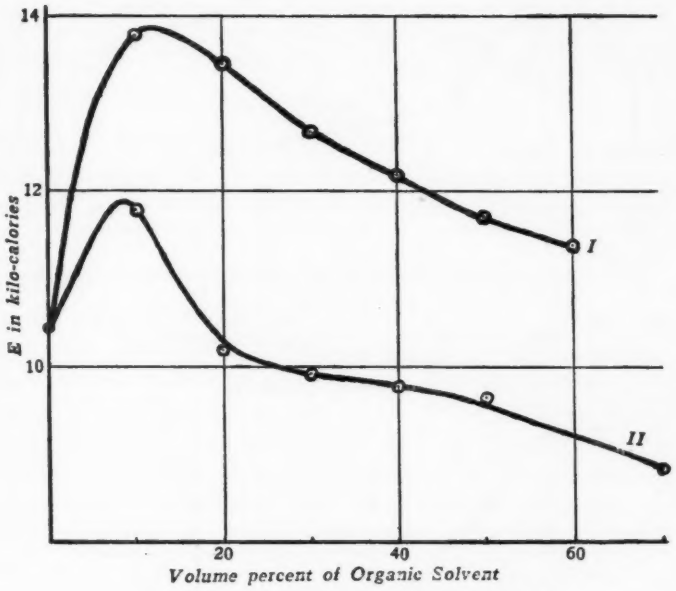

FIG. 3. Variation of E with composition

I. Dioxane-Water Mixtures
II. Acetone-Water Mixtures

Fig. 4 illustrates the variation of log PZ values with composition and brings out the remarkable parallelism between and trends of E and PZ values. Fairclough and Hinshelwood have shown, from statistical considerations, that the frequency factor (PZ) is a function of the characteristic frequency of the bond involved in a reaction and obtained a linear relationship between $\log_{10}$ PZ and $1/\sqrt{E}$ in a number of cases. Davis and Evans have observed a similar behaviour in the case of several aliphatic esters, the substituents being responsible for changes in activation energy. Fig. 5 shows the plots of $1/\sqrt{E}$ against $\log_{10}$ PZ for the present investigation. It is seen that they yield fairly linear plots. Combining these observations, it seems as though the behaviour referred to is independent of the agency (substituent or solvent

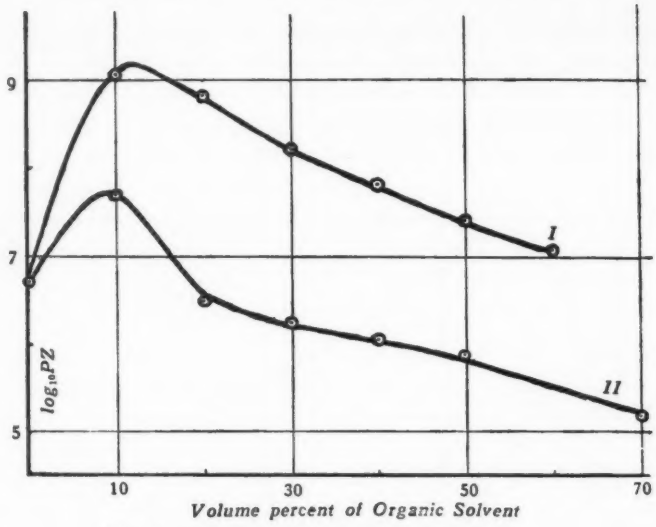

FIG. 4. Variation of log PZ with composition
I. Dioxane-Water Mixtures
II. Acetone-Water Mixtures

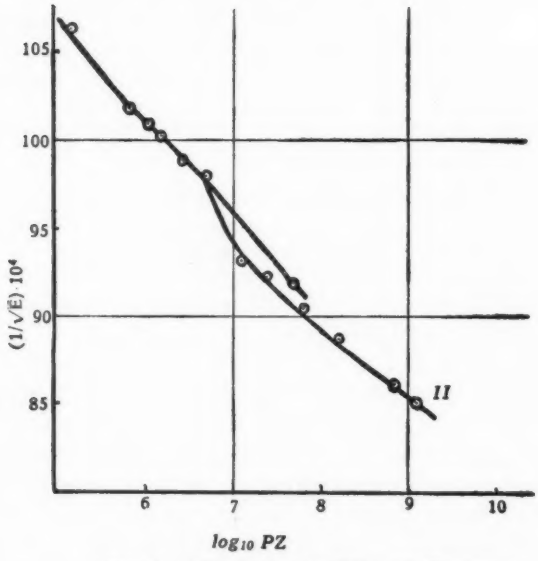

FIG. 5. Alk. Hydr.— log PZ — $1/\sqrt{E}$ curves
I. Acetone-Water Mixtures
II. Dioxane-Water Mixtures

change) that brings about changes in energies of activation and offers further support to the interpretation given by Fairclough and Hinshelwood.

Experimental

The materials used in the study were purified by the same procedure as described in the previous part.

Velocity Measurements.—The reaction vessels used were 100 ml. or 50 ml. Pyrex reaction bottles with specially ground stoppers. They were tested for evaporation losses by putting acetone in them and keeping for a month. The loss in weight was found to be negligible.

Owing to the fastness of the reaction, it had naturally to be studied at lower temperatures than in the case of acid hydrolysis and hence the temperature control possible was much better, the fluctuations being within $\pm 0{\cdot}005°$ C.

Ester solutions were prepared as described in Part III.

The alkaline hydrolysing agent was prepared in a similar way. The requisite amount of a previously standardised sodium carbonate-free sodium hydroxide solution required to make 100 ml. of N/10 solution was run into the appropriate volume of organic solvent taken in a 100 ml. standard flask and enough water added to bring the level a little below the neck. After allowing sufficient time (with occasional shaking) for the contents to attain room temperature, the solution was made up to the mark with water and well shaken.

The flasks containing ester solution and the hydrolysing agent were immersed in the thermostat and left for four hours for attainment of temperature equilibrium. The strength of the alkali solution was then determined by titration in order to evaluate the solvent expansion correction. The same correction was also applied to the ester solution. 50 ml. (or 25 ml.) or the alkali solution were transferred by means of a standard pipette into a 100 ml. (or 50 ml.) reaction bottle which was also kept immersed in the bath. After allowing a little more time to compensate for slight temperature changes, 50 ml. (or 25 ml.) of the ester solution were added to the alkali solution with a standardised rapid delivery pipette. The bottle was stoppered, taken out, well shaken and returned to the bath as quickly as possible. The instant of half-delivery of the ester solution was taken as zero time. The reaction was followed by withdrawing 10 ml. (or 5 ml.) samples of the reaction mixture and running them into 10 ml. (or 5 ml.) lots of N/20 HCl and titrating the excess of acid against N/40 barium hydroxide,

with bromo-thymol blue as indicator. Time was noted by a standardised stop-watch graduated to 0·2 sec. A second stop-watch of the same quality was employed for determining the reaction times for the samples accurately. Just before taking a reading, the second stop-watch was started at a definite time read in the first one. The second watch was stopped at the instant of half-delivery of the sample and the reading noted. The sum of the two gave the time for the particular sample. Half-deliveries were marked on the pipettes with a vibro tool. Typical runs are given in Tables IV and V.

The velocity constants were calculated from the equation for a second order reaction.

$$k(a-b)\,t = 2{\cdot}303\left[\log_{10}\frac{b}{a} + \log_{10}\frac{a-x}{b-x}\right],$$

TABLE IV

Alkaline hydrolysis of ethyl acetate in acetone-water mixtures at 30° C.

Vol. % acetone	Strength of alkali	Strength of ester	Titre of 10 ml. of acid used for stopping reaction						
				Time in sec. t	96·0	213·8	327·0	437·5	580·0	695·4
0	0·0497 N	0·0475 N	20·15	Titre of reaction mixture V_t	8·55	11·35	14·25	15·10	16·20	16·65
10	0·0499 N	0·0474 N	20·20	t	89·0	214·2	327·0	441·0	562·6	692·4
				V_t	8·05	12·15	14 05	15·02	16·00	16·50
20	0·0497 N	0·0476 N	20·20	t	92·0	210·0	329·8	445·6	579·8	723·0
				V_t	7·70	11·60	13·80	14·90	15·75	16·55
30	0·0497 N	0·0476 N	20·15	t	103·2	208·8	332·2	447·8	572·0	719·2
				V_t	7·45	10·72	13·15	14·25	15·10	16·00
40	0·0497 N	0·0486 N	19·70	t	73·5	213·0	327·5	435·0	552·1	648·9
				V_t	5·60	9·85	12·13	13·30	14·15	14·80
50	0·0496 N	0·0490 N	20·20	t	93·0	200·0	306·0	441·5	587·0	727·8
				V_t	5·70	9·05	11·30	12·90	14·10	15·20
70	0·0495 N	0·0486 N	20·20	t	77·2	187·0	296·4	409·4	521·2	652·6
				V_t	4·00	7·45	9·70	11·30	12·50	13·40

TABLE V

Alkaline hydrolysis of ethyl acetate in dioxan-water mixtures at 30° C.

Vol. % dioxan	Strength of alkali	Strength of ester	Titre for acid used (10 ml.) to stop reaction							
0	0·0497 N	0·0475 N	20·15	t	96·0	213·8	327·0	437·5	580·0	695·4
				Titre for V_t 10 ml. of reaction mixture	8·55	11·35	14·25	15·10	16·20	16·65
10	0·0503 N	0·0489 N	19·70	t	86·0	182·0	269·3	362·4	450·8	550·0
				V_t	7·65	11·10	13·0	13·95	14·50	15·50
20	0·0497 N	0·0487 N	19·70	t	90·3	181·2	275·0	384·4	478·4	585·4
				V_t	7·45	10·55	12·55	13·80	14·60	15·35
30	0·0498 N	0·0489 N	20·60	t	100·2	180·6	260·5	350·3	435·0	561·8
				V_t	7·72	10·40	12·50	13·70	14·45	15·53
40	0·0481 N	0·0493 N	20·60	t	94·2	175·6	281·2	364·0	445·0	550·6
				V_t	7·30	10·10	12·55	13·65	14·35	15·40
50	0·0495 N	0·0486 N	20·65	t	84·0	166·0	246·8	397·8	470·2	..
				V_t	5·75	8·75	10·70	12·30	13·65	..
60	0·0497 N	0·0495 N	19·70	t	91·5	190·5	306·2	404·2	489·9	633·2
				V_t	5·25	8·20	10·55	11·75	12·65	13·55

where a and b are alkali and ester concentrations and x the fraction hydrolysed at time t. Values of $\log_{10} \frac{a-x}{b-x}$ were plotted against t and k-values calculated from the slope of the straight lines obtained. This procedure for calculation eliminated any error in the noting of zero time. Fig. 6 gives a sample of the plot of $\log_{10} \frac{a-x}{b-x}$ against t.

SUMMARY

The alkaline hydrolysis of ethyl acetate in dioxane-water and acetone-water mixtures have been studied. The trend of the reaction rate shows a maximum in the region of 10% organic solvent except in the case of acetone-water mixtures at 30° C. A close parallelism is observed in the variations

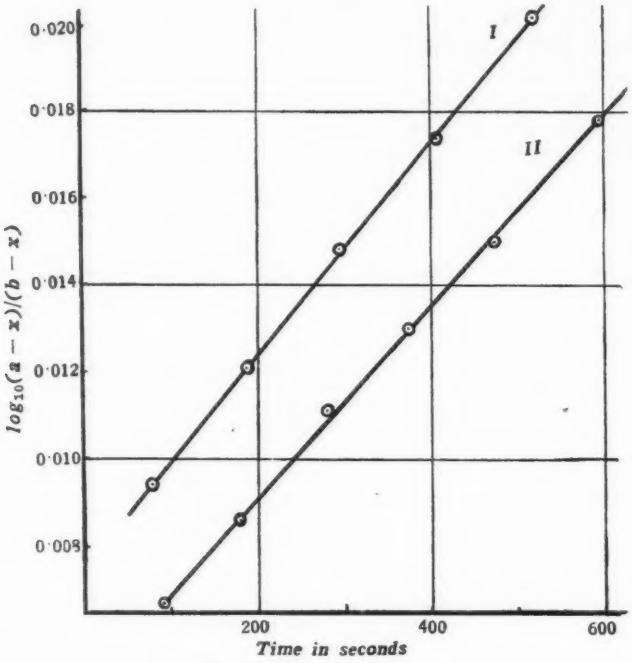

FIG. 6. 30° C. Alk. Hydr.
I. 70% Acetone ; II. 40% Dioxane.

of both E and $\log_{10}$ PZ values in the two series of solvent mixtures. Also, the PZ values have a marked tendency to follow changes in energies of activation.

REFERENCES

1. Davis, G. and Evans, D. P. .. *J. Chem. Soc.*, 1940, 339.
2. Fairclough, R. A. and Hinshelwood, C. N. *Ibid.*, 1937, 538.
3. Glasstone, Laidler and Eyring .. *Theory of Rate Processes*, McGraw Hill Book Co., 1941, 419.
4. Huang, T. C. and Hsieh, H. .. *J. Chin. Chem. Soc.*, 1939, **1**, 1.
5. Moelwyn-Hughes, E. A. .. *Kinetics of Reactions in Solution, O.V.P.*, 1947, 151.

VELOCITY OF SOUND IN METALS

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Recently developed methods of determining sound velocities in the sonic and ultrasonic regions have resulted in interesting observations being made in respect of certain substances. For instance, Druyvesteyn (1941) found that the velocity of sound shows a considerable variation in β brass according to the mechanical and heat treatment received by the specimen. Bordoni (1947) found that the sound velocity when plotted against the percentage impurity in aluminium in the range 100–99% aluminium shows a marked minimum at the 99·65% composition. Such investigations, when pursued in detail, are likely to be of interest from the point of view of both the technical and the academic aspects of metallurgy. Somewhat similar results were reported by Bez-Bardili (1935) with regard to the velocity of ultrasonic waves in aluminium. The following values are taken from his work:

Frequency	Mc/sec.	5·23	8·52	18·00
Ultrasonic velocity ..	m/sec.	5880	6150	6330

A marked dispersion of ultrasonic velocity (7·6%) in aluminium as we go from 5 to 18 megacycles is thus indicated. From another paper of Bez-Bardili (1935), it appears as if there is dispersion in copper and brass also. Certain preliminary investigations carried out at the Physics Department of the Andhra University, but unpublished, showed that no such effect could be established at least in the case of brass, if errors arising from the presence of boundaries and other similar causes are suitably eliminated.

The present investigation is taken up with a view to apply the newly developed wedge method of determining ultrasonic velocities to this problem and bring out the significance of coupling effects due to finite size in such studies. Experimental details of the method have been described in several earlier communications and will not be repeated here. A piezoelectric wedge is used as the source for ultrasonic waves and the Debye-Sears diffraction patterns are used to detect transmission frequencies. It is well known that thickness longitudinal vibrations in the case of a plate travel with a velocity which depends on the effective elastic constant and the density alone if the plate is of unlimited size. The velocity, unaffected by the boundaries, may thus be determined, in strict accord with theory only if we use infinitely extending plates, but this is not practicable. Use is, however, made of the fact that optimum thicknesses and sizes which reduce the boundary effects

to a minimum can be evolved. Several preliminary experiments have been performed by us in this direction and we have found that 2-inch square plates with thicknesses in the neighbourhood of 2 millimetres exhibit characteristics quite close to what may be expected of infinitely extending plates when we are working in the range of 1 to 10 megacycle frequencies. If the plate is too thin, flexural oscillations complicate the results and if the plate is too thick, the wavelength in the lower harmonic range becomes comparable to the lateral dimensions. The thickness of the plates used by us in the present investigation is worked up to being uniform to within 1 in 100. Our observations are in agreement with what has been recorded by Cady (1946) in his book, namely, " With thickness vibrations, this source of error is eliminated by observing at a high harmonic frequency. The lateral dimensions of the plate should be sufficiently great to avoid coupling with other modes and to permit the use of the theory of infinite plates. A safe minimum value for the ratio of lateral dimensions to half wavelength is perhaps 20." Results for three different thicknesses of aluminium and brass plates of the same size (2″ square) are given below.

Aluminium

Thickness of plate cm.	No. of harmonic n	Frequency mc./sec.	Frequency/n mc./sec.	Velocity of sound m./sec.	Mean velocity
·252	4	5·118	1·279	6446	6492
	5	6·476	1·295	6527	
	6	7·713	1·286	6480	
	7	9·044	1·292	6512	
	8	10·310	1·289	6495	
·203	4	6·384	1·596	6480	6525
	5	8·070	1·614	6552	
	6	9·672	1·612	6543	
·156	4	8·396	2·099	6548	6535
	5	10·460	2·092	6522	

Brass

·233	4	3·898	·9745	4542	4528
	5	4·858	·9716	4530	
	6	5·812	·9687	4516	
	7	6·781	·9687	4516	
	8	7·784	·9731	4537	
·202	4	4·504	1·126	4537	4524
	5	5·580	1·116	4511	
·158	4	5·792	1·448	4576	4569
	5	7·220	1·444	4562	

It will be noticed that the values for the first, second and third harmonics are not given in the results above. We have found that in the determination of velocity of sound in metals by the thickness vibrations of plates, it is preferable to use the higher harmonics rather than the fundamental and its second and third overtones. This observation is again similar to what has been observed by Cady (1946) and other investigators.

The figures in aluminium, as well as brass, show that the variation from the mean value in any particular case does not exceed about 1%. This is within the limit of experimental error as the thickness itself is uniform to only that order. We have thus to conclude that the valocity of sound is independent of frequency as well as of thickness of plates for brass and aluminium in the region of 1 to 10 megacycles, provided thicknesses likely to give rise to boundary effects and such other complications are avoided.

Summary

It has been experimentally shown, by applying the ultrasonic wedge method, that the sound velocity in brass and aluminium plates is independent of frequency in the range 1 to 10 megacycles. For obtaining this result unambiguously, one has to use plates of proper thicknesses and lateral dimensions and eliminate coupling and boundary effects.

References

1. Bez-Bardili .. *Phys. Zeit.*, 1935, **36**, 20.
2. ———— .. *Zeit. F. Phys.*, 1935, **96**, 761.
3. Bordoni, P. G. .. Publication No. 81, from the *Inst. Naz. Die Electroacustica*, Italy, 1947.
4. Cady, W. G. .. *Piezoelectricity*, 1946, 106 and 318.
5. Druyvesteyn, M. J. .. *Philips Technical Review*, 1941, **6**, 372.

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and Published by The Indian Academy of Sciences, Bangalore